A GAS CHROMATOGRAPHY/MASS SPECTROMETRY STUDY OF THE ALIPHATIC STRUCTURES OF COAL

1980

KENNETH WILLIAM CURRY

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The Pennsylvania State University

The Graduate School

Department of Chemistry

A Gas Chromatography/Mass Spectrometry Study of the Aliphatic Structures of Coal

A Thesis in

Chemistry

by

Kenneth William Curry

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of the Requirements
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The signatories below indicate that they approve the thesis of Kenneth William Curry.

ABSTRACT

Products from the trifluoroperoxyacetic acid oxidative degradation of 27 parent coal samples have been studied by gas chromatography and mass spectrometry. Structures have been tentatively assigned for the major products. These products show that 9,10-dihydroanthracene and 9,10-dihydrophenanthrene units are prominent features in most bituminous coals in accord with Given's structure of coal. Their frequency accounts for the fact that no continous fused ring structure or graphite structure exists. The only simple alkyl substituent is methyl.

Products from solvent refined coals incidates that liquefaction (solvent refining) sharply increases the amount of arylmethyl and aromatic structure and causes the appearance of unsubstituted phenyl groups. The increase in aromaticity is also demonstrated by model studies.

Nitric acid degradations have been investigated and have developed into a premier method for analyzing the amounts and lengths of linear alkane chains in coals.

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I. INTRODUCTION

The continuing problems in obtaining assured supplies of oil at a reasonable cost have resulted in a renewed interest in coal as a fuel source. In fact, processes for the production of synthetic fuels from coal were developed in Germany during World War II, and Sasol Incorporated has an on-line plant producing gasoline at this time in South Africa. Despite this success, there is still a surprising lack of knowledge concerning the organic structure and mineralogical composition of coal. Many of the problems encountered in characterizing coal and its derived products are due to the massive heterogeneity of this fossil fuel and the striking variations in rank and other parameters to be found between coals from different geographic regions and geological time periods. Compounded on this fact is that coals will vary in rank and other parameters within the same geographic region and geological time periods depending on the organic materials present and the conditions under which the coal is formed, temperature, pressure, solvents, etc.

This recent emphasis on the conversion of coal into substitute solid and liquid fuels has led to extensive research on the structural determinations of coal. The structure of coal has been studied by infrared spectroscopy, X-ray diffraction, UV spectroscopy, and degradative procedures which reduce the complex coal molecules into simple components.[1-8] Oxidation, destructive distillation, and solvent extraction of coal have given considerable information about the aromatic structures present. The studies of BF_3-phenol extracts

have given information about the types of alkyl side chains present in coal; however, these results are highly suspect.[9] Solid state ^{13}C NMR studies confirm the presence of both aliphatic and aromatic portions.[10] However, the aliphatic structures of coal are still unknown despite their key role in connecting aromatic domains. A technique suitable for studying the adiphatic structures as well as all structures of coal has been developed.[11] This technique involves the oxidative degradation of coal using a solution of 30% aqueous hydrogen peroxide and trifluoroacetic acid with concentrated sulfuric acid added to the reaction mixture. Coal reacts with this solution to produce colorless or pale brown solutions in which most of the aromatic structures have been destroyed and the aliphatic ones virtually untouched.[12,13] Volatile methyl esters can be obtained from this solution by concentrating the reaction mixtures by rotary evaporation and reacting the solutions with BF_3 and methanol. The methyl esters can be separated by gas chromatography.

The purpose of this thesis is to examine the products of the above oxidation process by way of gas chromatography coupled with chemical ionization and electron impact mass spectrometry to isolate and identify the products obtained from the oxidation of both parent and solvent refined coals.

II. HISTORICAL BACKGROUND

A. Trifluoroperoxyacetic Acid Oxidations

Trifluoroperoxyacetic (per TFA) was first prepared and studied by Emmons in 1953.[14] This peroxyacid was observed to have strong oxidizing power. It is formed by reacting trifluoroacetic acid (TFA) with aqueous hydrogen peroxide (H_2O_2). TFA reacts more rapidly with H_2O_2 than do formic or acetic acid and the equilibrium favors formation of the peroxyacid.

Per TFA is recognized as a possible source of the electrophilic hydroxyl cation, HO^+, by cleavage of the O-O bond to give $CF_3CO_2^-$ and HO^+. Per TFA has the ability to oxidize alkanes to yield alcohols and alkyl trifluoroacetates which are inert to further oxidation.[15,16] Pentane has been oxidized by using a 100 to 1 ratio of pentane to per TFA.[17] Deno and coworkers oxidized cyclohexane to cyclohexyl trifluoroacetate (78%) and cyclohexanol (0.3%) using a 1.2 to 1 ratio of hydrogen peroxide to cyclohexane.[15,16] Hydroxylation of alkyl chains remote from electronegative substituents has been demonstrated with 1-octanol and palmitic acid.[15,16] Attack remote from electronegative centers results from the electrophilic (HO^+) nature of per TFA. Small primary and secondary alcohols, carboxylic acid, esters and amides are inert to per TFA.[15,16]

Musgrave and coworkers first used trifluoroperoxyacetic acid to oxidize mesitylene to mesitol at low conversions.[18] Other benzene analogs were reacted with 1.5 equivalents of per TFA to give mixtures

of phenols and quinones with 30-40% conversion. Oxidation of m-xylene results in 2,6-xylenol, 2,4-xylenol, and m-xyloquinone.

Hart and coworkers added a Lewis acid, BF_3, to trifluoroperoxyacetic acid and obtained mesitol from mesitylene in quantitative yields.[19] They also oxidized highly substituted alkylbenzenes such as hexamethylbenzene which gave 2,3,4,5,6,6-hexamethyl-1,2,4-cyclohexadienone. Alkylbenzenes that were less substituted, such as toluene, gave tars when reacted with limited amounts of TFA-H_2O_2-BF_3. The tars most likely resulted from further attack by per TFA on the phenols formed. This work demonstrates the preference of per TFA to attack benzene rings over benzylic hydrogen.

Numerous alkylbenzenes were reacted with per TFA by Mr. Stephen Stroud. The reaction of excess H_2O_2 in TFA with alkylbenzenes (12-20 mol H_2O_2 per mol alkylbenzene) resulted in the complete oxidation of the aromatic ring leaving a carboxyl group attached to the aliphatic chain.[11-13] For example, toluene was oxidized to acetic acid, cyclohexylbenzene to cyclohexanecarboxylic acid, and 1,3-diphenylpropane to glutaric acid.[20] This is in contrast to other oxidizing reagents [HNO_3, O_2, Mn(VII), Cr(VI)] which attack the benzylic position of alkylbenzenes to form benzoic acid.

Ms. Barbara A. Greigger, in early work on model compounds, demonstrated that oxidation of alkylbenzenes with TFA-H_2O_2 produced products arising from migration of hydrogen, notably acetic acid.[21] For example, compounds without arylmethyl groups such as diphenylmethane and 9,10-dihydroanthracene formed acetic acid as a major product. Since it was desired to use the per TFA oxidation method

as an analytical tool for studying aliphatic structures of coal, formation of acetic acid from hydrogen migration needed to be eliminated. Addition of concentrated sulfuric acid to trifluoroperoxyacetic acid reaction mixtures eliminated the products arising from hydrogen migration. Furthermore, the addition of sulfuric acid decreased the amount of other side products and increased yields of the major products.

Deno and coworkers have shown that coal reacts with a solution of per TFA and H_2O_2 to produce colorless or pale brown solutions in which most of the aromatic structures have been destroyed and the aliphatic ones largely untouched.[12,13] Similarly, addition of sulfuric acid to per TFA reactions of coal resulted in a decrease of the amount of acetic acid and an increase in the amount of succinic acid.

B. Structure of Coal

It is a general concensus that coal is a compact, polymeric mass of plant debris composed of carbon, hydrogen, oxygen, nitrogen, sulfur, and small quantities of inorganic material. The structure of coal has been extensively studied by X-ray diffraction; UV, IR, and NMR spectroscopy; oxidation, destructive distillation; and specific group analysis.[1-10] These studies indicate the presence of both aliphatic and aromatic portions in coal. Estimates of the percent aromatic carbon content have been made. Brown coal and lignite (60-70% carbon) are soft coals and have approximately 40% aromatic carbon. Bituminous coal (70-92% carbon) is harder and has 60% aromatic carbon.

Anthracite (92-95% carbon), the hardest of all coals, has 96% aromatic carbon. The majority of the structural studies have been carried out on bituminous coals. Studies can be done either on the intact coal or on degraded fragments. Due to the size and complexity of coal, degradation simplifies the studies.

Coal is considered to have been formed from the peat deposits produced in swamps through the accumulation of plant substances. These substances contained distinctive organic chemical structures such as cellulose and lignins. The plant substances were subjected to various processes such as compaction by subsequent sediments and heating. These conditions of pressure and temperature account for the coalification of the plant matter. The relative magnitude or severity of the conditions lead to increasing coal rank. For most purposes, the various coals can be arranged in rank order:

	Peat	Increasing
	↓	carbon
Increasing Rank	Brown coal/lignite	decreasing
	Subbituminous coal	hydrogen
	Bituminous coal	and oxygen
	↓	
	Anthracite coal	

Many physical and chemical properties vary with rank, but this variation is not a simple progression.[22]

The concept of coal structure is difficult to define as the macromolecules of coal are not composed of repeating monomeric units (as in, for example, the proteins). The problem is one of assigning a structure to a mixture; however, coal can be described in terms of

structural parameters. These may include:

1. Size distribution of the macromolecules
2. Degree of cross linking
3. Type of cross linking
4. Carbon aromaticity
5. Average size of condensed aromatic units
6. Number of hydroxyl groups
7. Scissile bridging structures

The above list is neither exhaustive nor necessarily correct; it is based on the assumption that coal has a polymeric character; that it does, in fact, consist of macromolecules.[22]

Various experimental techniques have given results that suggest the presence of certain types of structures in coal.[1-4,6-10,23-27] For the bituminous coal, the following structural units have been proposed:

1. There are more arylmethyl groups present than arylethyl, propyl and butyl groups. Groups longer than butyl are not very likely.
2. All hydroxy groups are phenolic.
3. Methoxy groups are not present.
4. There are more carbons present with zero or one hydrogen than carbons with two or three hydrogens.
5. A total of 20-60% of the hydrogen is aliphatic in a typical bituminous coal.

Using these and other pieces of information, a generalized concept of the structure of bituminous coal was proposed by Given.[23,24] He postulated that coal is made up of many aromatic nuclei that are

linked together by hydroaromatic bridges. The bridges were first proposed to be methylene, making up 9,10-dihydroanthracene structures.[23] However, he later changed his proposed structure to 9,10-dihydrophenanthrene units to better account for experimental results.[24]

The aromatic/hydroaromatic model is the "generally accepted" model and it represents a picture of a skeletal structure which consists of clusters of condensed aromatic nuclei. The size of the clusters ranges from one ring to several but on the average is about three rings for coals between 80 and 90% carbon. Above 90% carbon the cluster size increases rapidly as the anthracites are approached. The clusters are connected by hydroaromatic linkages with a small number of heteroatom (mainly oxygen) linkages.

The hydroaromatic model has not been directly tested or confirmed and has arisen largely because it appears to be a "reasonable" interpretation of the parameters of coal structure. However, there appears to be new evidence which strongly suggests that the hydroaromatic model is largely correct for the majority of coals. Recent work by Deno and coworkers has shown that hydroaromatic molecules are excellent models for coal under the conditions of oxidative degradation by trifluoroacetic acid.[28] This work, which is still continuing, suggests that hydroaromatic structures are the necessary precursors of the reaction products obtained. The similarity between 5,12-dihydro-naphthacene and the "monomer" proposed by Given (1960) is very striking indeed.

III. EXPERIMENTAL PROCEDURES AND RESULTS

A. Instrumental Techniques

1. Gas Chromatography (GC)

Gas chromatograms were recorded on a Finnigan 9500 gas chromatograph equipped with a flame ionization detector. The carrier gas was helium and the fuel gas was a mixture of air and hydrogen. A 6 ft, 0.25 inch O.D. x 2 mm I.D. U-shaped column was used. The packing material was 3% OV-17 (50-50 Me-Ph silicone) on 80/100 mesh Supelcoport C. Columns and packing materials were purchased from Supelco, Inc., Bellefonte, PA.

An initial comparison test was run comparing column and capillary GC. Although the capillary GC gave better separation and sharper peak shapes, it was noted that the 0.25 inch diameter, 6 ft U-shaped column gave adequate separation for the samples under study. Therefore, due to being easier to use, the U-shaped column was chosen for use in this study. Another comparison study was run comparing supporting phases. Columns of 3% SP-2100 (100% Me silicone) on 80/100 Supelcoport C, 3% OV-1 (100% Me silicone) on 80/100 Gas Chrom Q, and 3% OV-17 (50-50 Me-Ph silicone) on 80/100 Supelcoport C were compared and the 3% OV-17 gave the better separation and peak shapes for the samples under study. Since the GC peaks were to be integrated by hand, a survey was run varying the chart recorder speed and temperature program to be able to broaden the peaks as much as possible in order to increase accuracy in integration while maintaining separation of the compounds. This

survey produced the results of a chart recorder speed of one inch per minute and a temperature program rate of 50-250°C at 10°C per minute to give the desired peak shape.

All columns used were hand packed, conditioned and tested with a standard sample of methyl esters before use and the same column was used for each set of data obtained in order to maintain conditions as nearly the same as possible.

2. Gas Chromatography/Mass Spectrometry (GC/MS)

a. Chemical Ionization Mass Spectrometry (CIMS). Spectra of all samples were recorded using a Finnigan 3200 chemical ionization mass spectrometer coupled to a Model 6000 MS data system. The carrier gas was methane and the same column and temperature program were used to provide better comparison to the gas chromatograms for identification of the peak molecular weight.

From these spectra, determinations of the molecular weight of the methyl esters can be determined by way of the characteristic peaks of:

$$P + 1 = P + H^+$$

$$P + 29 = P + C_2H_5^+$$

$$P + 41 = P + C_3H_5^+$$

$$P - 32 = P + H - CH_3OH$$

From these the molecular weight of P can be assigned and the products recognized as methyl esters.

b. Electron Impact Mass Spectrometry (EIMS). Spectra were recorded on a Finnigan 6000 MS data system equipped with an electron impact detector. The carrier gas was helium and the same column and temperature program were used for better comparison to the gas chromatograms.

From the M/E peaks of these spectra the following characteristic peaks were noted:

P - MW of the compound (not always seen)

P - 31 - Loss of MeO

P - 59 - Loss of one acid group (CO_2Me)

P - 118 - Loss of two acid groups

P - 177 - Loss of three acid groups

Plus other fragmentations characteristic of the compounds under study.

From these spectra and the molecular weight determinations from the CI spectra, a probable structure for the compound can be devised.

3. Other Analytical Techniques Used

To aid in the identification of the GC peaks, the following analytical techniques were used:

1. BF_3/deuterated MeOH studies to determine the number of carboxylic acid groups present

2. Model studies (comparison of EI spectra)

3. High resolution mass spectrometry (gives elemental compositions)

4. Comparison of GC retention times to and spiking samples with authentic compounds (aids compound identification)

5. Comparison of unknown EI spectra to standard spectra.

B. Coals, Solvent Refined Coals and Models

All parent coals with the exception of POC-339, POC-340, DJR-29, DJR-70, DJR-44 and DJR-47 were obtained from the Penn State/DOE coal sample base, assembled under the direction of Dr. William Spackman. The coal samples of POC-339, POC-340, DJR-29, DJR-70, DJR-44 and DJR-47 were furnished by Dr. D. D. Whitehurst of Mobil Research and Development Corp. Computer print outs listing petrographic, proximate and ultimate analyses were obtained for each Penn State/DOE coal sample base sample. The elemental analyses of the parent coal samples appear in Table 1.

The solvent-refined coal samples, before, after three minutes, after 90 minutes and residues from the three-minute solvent refining, were obtained from Dr. D. D. Whitehurst of Mobil Research and Development Corp. The parent coals were bituminous and had been originally obtained from the Penn State coal base and carry their code numbers. The solvent-refined coals were prepared by heating the coals in tetralin at 400°C and at 1000 psi of hydrogen gas for three minutes and 90 minutes. The effect of this was to lower the sulfur content, remove mineral matter and convert the coal to a low melting solid which is soluble in organic solvents. The residue samples were the residues after three minutes of solvent refining.

Table 1. Parent Coal Elemental Analysis[a]

Province	Sample	State	Name	% N	% C	% H	% S	% O	Rank	C/H Ratio (By Wt.)
Eastern	DJR-71 (PSOC-256)	PA	PA Lower Freeport	1.86	82.59	4.28	0.51	5.96	MED	1.608
	DJR-67 (PSOC-330)	PA	PA Middle Kittaning	1.71	76.93	5.09	0.67	7.86	HVB	1.259
	PSOC-349	PA	PA Lower Clarion	1.44	73.21	5.24	5.64	4.39	HVA	1.164
	PSOC-124	WV	WV Lower Kittaning	1.25	75.78	6.33	0.99	6.27	HVA	0.998
	PSOC-372	KY	KY Imboden	1.24	80.41	5.22	1.28	6.32	HVA	1.284
	PSOC-308	OH	OH #5	1.57	69.57	5.00	4.34	9.32	HVB	1.160
Interior	PSOC-641	KY	KY #6	1.44	74.68	5.10	2.10	7.58	HVA	1.220
	DJR-47	IL	IL #6 Monterey	1.08	69.72	4.98	5.14	8.20	HVC	1.167
	DJR-44	IL	IL #6 Burning Star	1.39	70.53	5.12	1.62	9.46	HVC	1.148
	PSOC-582	IL	IL #5	1.05	67.60	4.83	5.39	7.88	HVB	1.166
	PSOC-399	OK	OK Fort Scott	1.57	74.29	5.42	3.90	6.75	HVA	1.142
	DJR-69 (PSOC-405)	OK	OK Lower Hartshorng	1.48	81.49	4.29	0.61	2.89	LOW	1.583
Rocky Mountain	PSOC-155	UT	UT Mesa Verde	1.05	56.87	5.36	1.54	10.44	HVC	0.884
	PSOC-453	UT	UT Blind Canyon	1.37	76.14	5.88	0.51	10.62	HVA	1.080
	PSOC-459	UT	UT Lower Sunnyside	1.36	74.92	5.49	0.90	8.98	HVB	1.137
	PSOC-500	UT	UT Hiawatha	1.09	70.76	5.38	0.80	10.88	HVB	1.096
	PSOC-503	UT	UT Upper Sunnyside	1.38	76.39	5.20	0.67	8.01	HVA	1.224
	DJR-66 (PSOC-312)	AZ	AZ Red	1.30	72.58	5.38	0.29	13.55	HVC	1.124
	PSOC-450	CO	CO Upper B	1.78	78.85	5.31	0.88	5.89	MED	1.237

Table 1. (continued)

Province	Sample	State	Name	% N	% C	% H	% S	% O	Rank	C/H Ratio (By Wt.)
Great Plains	DJR-70	ND	ND Lignite	0.92	65.32	4.37	0.29	20.66	LIG	1.246
	DJR-29	WY	Wyodak	0.90	71.82	5.20	0.30	17.12	SBA	1.151
	PSOC-535	MT	MT Dietz	0.95	70.19	4.66	0.91	15.03	SBA	1.255
Gulf	PSOC-418	TX	TX Lignite	0.92	50.71	4.48	0.81	15.57	LIG	0.943
	PSOC-623	TX	Darco TX Lignite	1.07	60.67	4.27	0.84	14.28	LIG	1.184
Pacific	PSOC-95	WA	WA Queen #4	0.83	64.38	4.78	1.42	7.46	HVA	1.122
Alaskan	DJR-37 (POC-339)	AK	Alaskan	----	63.03	5.22	----	----	SB	1.006
	DJR-39 (POC-340)	AK	Alaskan	----	65.87	5.16	----	----	SB	1.064

[a]Given on a dry weight basis.

C. Trifluoroperoxyacetic Acid/Sulfuric Acid Oxidations

1. Oxidation of Parent Coals

To a round-bottom flask fitted with a water-cooled condensor and a magnetic stirring bar, 5 ml of trifluoroacetic acid are added. Stirring is started and 10 ml of 30% aqueous H_2O_2 added. After two minutes, 4 ml of 97% H_2SO_4 is added. Some heat is generated and it requires about five minutes for the temperature to return to 25°C.

The condensor is replaced by a powder funnel and 0.5 g of the -20 mesh coal is added. The condensor is returned to the flask. After 2-5 minutes of stirring, an exothermic reaction starts and the temperature rises to 70°C. The temperature is allowed to decline for one hour while the contents are stirred. After one hour of reaction time, a KI test for peroxides is generally negative. At this point, 4 ml of 30% aqueous H_2O_2 is added and stirring continued at 60°C for four hours. A KI test is positive at this time.

The excess peroxide is destroyed by adding 100 mg of 10% Pt on asbestos. When a KI test becomes negative, the Pt is removed by filtration. The filtrate is distilled at 2 KPa and 90°C to remove water and volatile materials. The nonvolatile fraction is stirred at 60°C for two hours with 6 ml of 14% BF_3 in methanol to form the methyl esters. The methyl esters are dissolved in CH_2Cl_2 and the solution is washed once with 10% $NaCO_3$ and twice with water. After drying over $MgSO_4$, the solution is decanted and the CH_2Cl_2 removed on a rotary evaporator.

Twenty-seven parent coals were oxidized using the above procedure and examined by way of gas chromatography and GC/MS. One hundred four separate compounds were detected in the 27 samples, averaging 30-40 compounds per sample. The results of this study are given in Table 1 of the Appendix. Fifty-three compounds were chosen as the major components of the coal samples and the most probable structures determined. The results are reported as Table 2. The relative percent total GC areas are reported as Table 3, along with the percent total GC area accounted for by these 53 compounds.

2. Oxidation of Solvent-Refined Coals

The procedure was the same as in the parent coals except for the second addition of H_2O_2. It was found that the KI test was positive after the first hour and at the end of four hours of reaction time and the second addition of H_2O_2 was not needed. This is believed to be due to metal ions in the parent coals catalyzing the decomposition of the peroxides. Also, the isolation of the methyl esters was made more quantitative by modifying the procedure for isolation. After esterification with BF_3 in methanol, 100 ml of saturated aqueous NaCl was added and the mixture extracted with three 35-ml portions of CH_2Cl_2. The combined CH_2Cl_2 extracts were washed with 100 ml of 3% $NaHCO_3$ followed by washing with saturated aqueous NaCl. A weighed amount of acetophenone was added as an internal standard.

Five parent coals, their three-minute and 90-minute SRC's and the residue from the three-minute SRC were oxidized using the above procedure. The samples were analyzed using GC/MS and 52 compounds

Table 2. Structures of Parent Coal PTFA Oxidation Products

MW = 132 Propanedioic Acid[a,b] $X-CH_2-X$	MW = 160 Pentanedioic Acid $X-(CH_2)_3-X$
MW = 144 Cis-butenedioic Acid $X-CH=CH-X$	MW = 162 2-Hydroxybutanedioic Acid $X-CH(OH)-CH_2-X$
MW = 146 Butanedioic Acid $X-CH_2-CH_2-X$	MW = 174 Hexanedioic Acid $X-(CH_2)_4-X$
MW = 160 2-Methylbutanedioic Acid $X-CH(Me)-CH_2-X$	MW = 188 Heptanedioic Acid $X-(CH_2)_5-X$
MW = 176 2-Methoxybutanedioic Acid $X-CH_2-CH(OMe)-X$	MW = 204 2-Carboxybutanedioic Acid $X-CH_2-CH(X)-X$

Table 2. (continued)

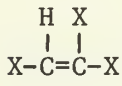
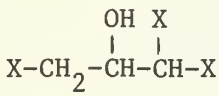
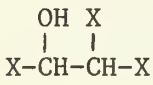
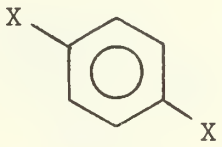
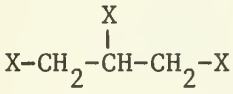
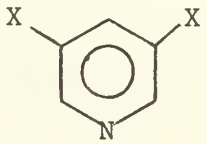
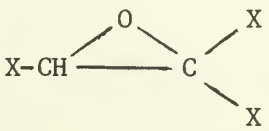
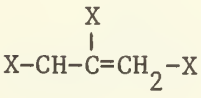
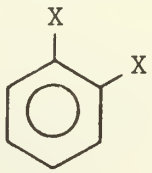
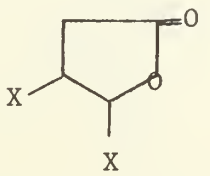
MW = 202A 2-Carboxybutenedioic Acid 	MW = 234 x-Carboxy-y-hydroxy-pentanedioic Acid 
MW = 220 2-Carboxy-3-hydroxy-butanedioic Acid 	MW = 194B Benzene-1,4-dicarboxylic Acid 
MW = 218A 3-Carboxypentanedioic Acid 	MW = 195 Pyridine-x,y-dicarboxylic Acid (two isomers) 
MW = 218B Oxiranetricarboxylic Acid 	MW = 216A 3-Carboxy-2-pentenedioic Acid 
MW = 194A Benzene-1,2-dicarboxlic Acid 	MW = 202B x,y-Dicarboxybutanolide (two isomers) 

Table 2. (continued)

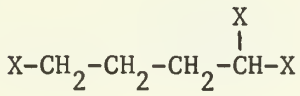
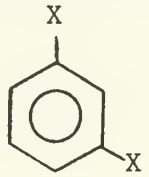
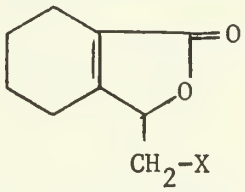
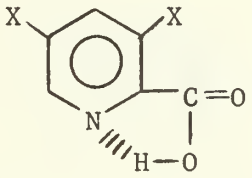
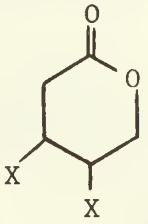
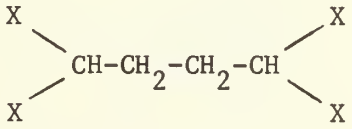
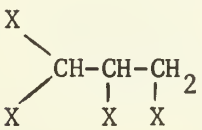
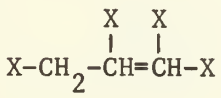
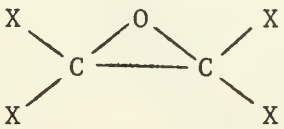
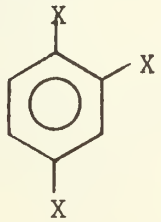
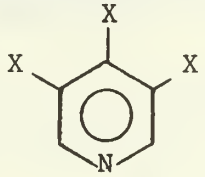
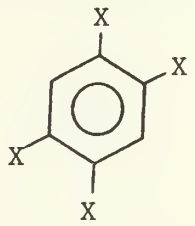
MW = 232 x-Carboxyhexanedioic Acid (three isomers) 	MW = 194C Benzene-1,3-dicarboxylic Acid 
MW = 210 4,5,6,7-Tetrahydrophthalide-3-acetic Acid[c] 	MW = 239 Pyridine-2,x,y-tricarboxylic Acid 
MW = 216B x,y-Dicarboxypentanolide 	MW = 290 x,y-Dicarboxyhexanedioic Acid (two isomers) 
MW = 276A 2,3-Dicarboxypentanedioic Acid 	MW = 274 x,y-Dicarboxy-2-pentenedioic Acid 
MW = 276B Oxiranetetracarboxylic Acid 	MW = 252A Benzene-1,2,4-tricarboxlic Acid 

Table 2. (continued)

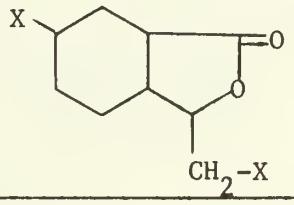
MW = 253 Pyridine-x,y,z-tricarboxylic Acid



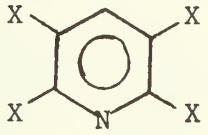
MW = 310A Benzene-1,2,4,5-tetracarboxylic Acid



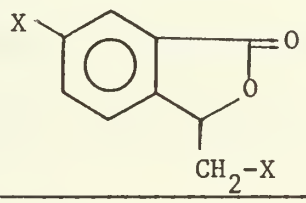
MW = 268 x-Carboxy-4,5,6,7-tetrahydrophthalide-3-acetic Acid (three isomers)



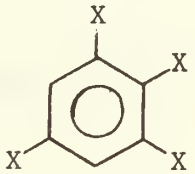
MW = 311 Pyridine-2,x,y,z-tetracarboxylic Acid



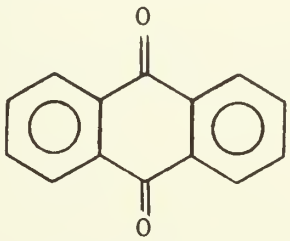
MW = 264 x-Carboxyphthalide-3-acetic Acid



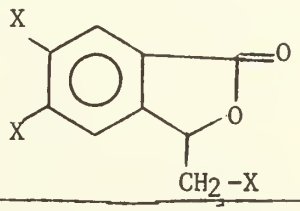
MW = 310B Benzene-1,2,3,5-tetracarboxylic Acid



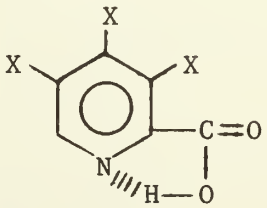
MW = 208 Anthraquinone



MW = 322 x,y-Dicarboxyphthalide-3-acetic Acid



MW = 297 Pyridine-2,x,y,z-tetracarboxylic Acid



MW = 308 x,y-Dicarboxyphthalide-3-carboxylic Acid (two isomers)

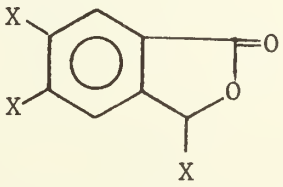
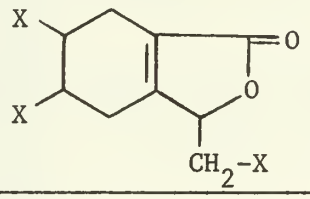
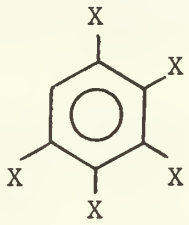
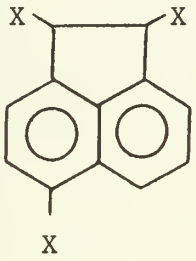
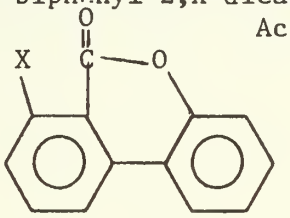


Table 2. (continued)

MW = 326 x,y-Dicarboxy-4,5,6,7-tetrahydrophthalide-3-acetic Acid 	MW = 368 Benzene-1,2,3,4,5-pentacarboxylic Acid 
MW = 328 Acenaphthene-1,2,5-tricarboxylic Acid 	MW = 254 Lactone of 2'-hydroxy-biphenyl-2,x-dicarboxylic Acid 

[a]X = CO_2Me

[b]All products are named for the corresponding acid.

[c]Phthalide = 1(3H)-isobenzo-furanone.

Table 3. Major Components of PTFA Oxidations of Parent Coals

Province	Sample	132 (4.36)	144 (5.64)	146 (6.04)	160 (6.52)	176 (7.24)	160 (7.52)	162 (7.98)	174 (9.20)
Eastern	DJR-71 (PSOC-256)	10.9	1.3	3.4	---	0.5	---	0.6	---
	DJR-67 (PSOC-330)	29.1	0.2	6.1	1.1	0.8	1.3	1.0	0.1
	PSOC-349	---	---	0.4	---	---	1.0	1.0	---
	PSOC-124	19.7	1.5	17.2	---	---	5.7	---	0.6
	PSOC-372	---	---	---	---	---	---	---	---
	PSOC-308	---	---	0.2	---	1.0	---	0.9	---
Interior	PSOC-641	---	---	---	---	---	---	---	2.0
	DJR-47	16.2	0.6	2.5	---	2.3	1.4	1.6	0.3
	DJR-44	3.7	0.7	2.5	3.2	---	2.9	3.7	---
	PSOC-582	---	---	---	---	---	---	---	---
	PSOC-399	---	---	0.1	0.7	---	0.6	1.6	---
	DJR-69 (PSOC-405)	6.2	0.5	8.3	1.7	2.1	---	2.4	0.7
Rocky Mountain	PSOC-155	---	---	---	---	---	---	---	---
	PSOC-453	11.9	1.3	10.0	2.5	---	1.9	---	0.3
	PSOC-459	7.9	0.8	9.3	1.7	---	1.2	---	---
	PSOC-500	11.2	---	8.9	2.7	---	2.1	1.9	---
	PSOC-503	---	---	---	0.6	---	0.5	0.3	---
	DJR-66 (PSOC-312)	16.4	1.4	10.1	1.3	1.6	---	6.1	---
	PSOC-450	0.4	---	0.3	---	---	0.2	---	---
Great Plains	DJR-70	4.2	1.6	8.7	2.2	---	6.0	0.5	---
	DJR-29	---	---	0.9	---	0.6	2.9	3.1	---
	PSOC-535	10.6	2.0	12.0	3.1	---	3.3	0.4	0.4
Gulf	PSOC-418	---	---	---	---	---	---	---	---
	PSOC-623	2.0	---	1.8	---	---	0.3	---	---
Pacific	PSOC-95	16.4	---	8.5	1.4	---	3.7	0.3	0.2
Alaskan	DJR-37 (POC-339)	4.1	---	3.4	2.0	---	2.0	0.8	0.3
	DJR-39 (POC-340)	0.5	---	1.4	4.5	---	5.7	---	1.4

Table 3. (continued)

Sample	188 (10.12)	204 (10.49)	202A (11.27)	220 (11.46)	218A (11.82)	218B (12.32)	194A (12.62)	232 (12.63)	234 (12.78)
DJR-71 (PSOC-256)	0.4	13.4	0.7	2.5	4.7	11.3	---	5.9	---
DJR-67 (PSOC-330)	0.4	12.7	0.6	2.8	4.6	13.2	---	---	3.6
PSOC-349	1.2	14.3	---	3.6	7.8	5.8	5.5	---	---
PSOC-124	---	4.3	---	2.0	11.3	5.9	---	2.3	0.8
PSOC-372	---	1.6	1.9	---	10.9	2.7	1.0	---	1.2
PSOC-308	0.6	8.8	1.8	3.8	10.9	4.0	1.7	---	3.2
PSOC-641	---	9.7	---	3.0	5.1	15.4	---	4.7	---
DJR-47	1.6	10.8	0.9	2.2	5.3	17.7	---	3.1	---
DJR-44	3.1	11.5	1.7	3.1	8.7	11.2	---	5.4	---
PSOC-582	2.8	14.5	0.2	2.1	5.0	19.9	---	1.6	3.9
PSOC-399	1.0	9.0	1.5	2.5	5.1	4.7	---	3.5	---
DJR-69 (PSOC-405)	---	2.7	2.2	---	9.1	6.4	6.5	---	1.3
PSOC-155	---	---	---	---	3.6	2.2	---	2.0	---
PSOC-453	---	4.0	0.8	---	3.4	3.8	0.7	---	---
PSOC-459	---	2.1	1.6	---	4.6	2.8	2.1	---	---
PSOC-500	---	4.6	1.2	2.4	5.7	10.4	---	4.2	---
PSOC-503	---	7.9	---	1.6	6.8	14.6	---	7.6	---
DJR-66 (PSOC-312)	---	4.7	1.5	---	6.6	2.8	---	---	2.5
PSOC-450	---	2.1	1.5	---	5.7	3.9	1.9	---	---
DJR-70	0.4	12.6	0.6	0.6	7.5	9.3	---	8.6	5.1
DJR-20	---	---	3.5	---	10.0	3.8	---	3.4	3.3
PSOC-535	---	4.8	2.4	---	6.2	7.0	---	4.4	---
PSOC-418	---	12.9	3.6	---	15.4	13.0	---	---	2.9
PSOC-623	0.5	2.7	---	0.3	1.5	3.5	---	2.1	---
PSOC-95	---	9.3	1.7	---	5.2	7.1	---	3.1	---
DJR-37 (POC-339)	---	3.3	3.1	---	10.8	13.1	---	---	3.6
DJR-39 (POC-340)	---	10.7	0.4	1.2	6.3	8.7	---	8.4	---

Table 3. (continued)

Sample	194B (12.93)	195 (13.01)	216A (13.23)	232 (13.32)	202B (13.43)	194C (13.62)	202B (13.79)	195 (13.84)	210 (13.92)
DJR-71 (PSOC-256)	---	0.9	0.8	---	1.6	---	---	---	2.5
DJR-67 (PSOC-330)	---	---	0.5	---	0.6	---	---	0.3	---
PSOC-349	---	---	2.2	---	---	---	0.4	---	---
PSOC-124	---	---	---	1.0	---	---	---	---	---
PSOC-372	---	0.8	1.6	---	---	---	0.8	---	1.8
PSOC-308	---	3.3	2.3	2.4	---	---	---	2.5	---
PSOC-641	---	---	---	7.6	---	---	---	---	2.6
DJR-47	---	0.4	---	---	---	---	0.1	---	2.4
DJR-44	4.5	---	---	---	---	---	---	---	2.6
PSOC-582	---	---	---	---	---	---	1.2	---	3.4
PSOC-399	---	---	1.1	---	---	---	---	1.8	2.1
DJR-69 (PSOC-405)	2.6	---	---	---	1.9	---	---	---	4.9
PSOC-155	---	---	---	0.3	---	---	---	0.3	---
PSOC-453	3.5	---	---	0.9	1.5	7.4	---	---	---
PSOC-459	2.2	---	1.2	---	---	7.4	0.9	---	---
PSOC-500	---	---	0.5	0.4	1.2	---	0.5	---	---
PSOC-503	---	---	1.9	---	2.1	---	1.4	---	---
DJR-66 (PSOC-312)	---	---	3.5	---	---	---	0.6	---	0.7
PSOC-450	---	2.9	1.1	1.3	---	---	---	1.4	---
DJR-70	---	---	2.5	---	---	---	0.3	---	---
DJR-20	---	---	2.0	4.2	2.5	---	1.2	---	---
PSOC-535	0.9	---	---	1.7	1.8	---	---	---	1.9
PSOC-418	---	---	3.1	---	---	---	0.9	1.9	---
PSOC-623	---	---	---	0.1	0.3	---	---	---	0.1
PSOC-95	---	0.7	0.8	---	0.9	---	---	---	1.8
DJR-37 (POC-339)	---	---	1.3	---	0.9	---	1.1	---	---
DJR-39 (POC-340)	---	---	2.2	---	---	---	---	---	---

Table 3. (continued)

Sample	232 (14.26)	216A (14.58)	216B (14.80)	276A (15.20)	276B (15.77)	239 (16.07)	290 (16.40)	290 (16.68)	274 (16.97)
DJR-71 (PSOC-256)	---	1.3	---	1.8	7.4	---	---	---	---
DJR-67 (PSOC-330)	1.7	1.7	0.1	1.3	5.4	---	0.5	0.5	0.1
PSOC-349	1.0	1.2	1.0	1.3	5.8	---	1.3	1.7	1.2
PSOC-124	---	---	1.0	0.4	2.9	---	0.6	1.0	0.2
PSOC-372	---	0.5	2.4	---	4.7	0.9	1.3	---	0.7
PSOC-308	---	1.7	3.7	---	6.8	---	1.9	1.3	1.0
PSOC-641	---	3.0	---	2.3	5.0	---	2.2	4.1	1.9
DJR-47	0.5	1.9	0.1	1.7	7.2	---	1.3	2.2	---
DJR-44	---	---	---	3.8	4.7	---	1.4	2.1	---
PSOC-582	0.9	---	---	0.6	17.0	---	0.6	2.9	1.2
PSOC-399	2.1	1.7	---	1.1	9.3	---	1.0	2.8	0.8
DJR-69 (PSOC-405)	---	2.1	0.2	---	4.7	---	0.8	0.5	---
PSOC-155	1.7	1.7	0.1	---	---	---	---	1.0	---
PSOC-453	---	1.6	---	---	2.9	---	0.1	0.2	---
PSOC-459	0.3	---	---	---	1.5	0.8	0.6	---	---
PSOC-500	0.4	1.3	---	0.2	6.4	---	1.6	1.6	---
PSOC-503	1.7	1.3	2.1	---	9.9	---	1.0	1.4	---
DJR-66 (PSOC-312)	---	0.6	2.5	0.5	5.8	---	1.0	---	0.4
PSOC-450	1.4	1.6	---	---	4.2	2.1	0.6	---	---
DJR-70	---	0.3	1.2	0.8	11.6	---	1.5	0.4	1.4
DJR-20	4.1	4.4	1.8	---	11.9	---	1.9	---	5.8
PSOC-535	---	1.5	0.2	---	3.0	---	1.1	1.1	0.3
PSOC-418	---	2.1	4.0	1.8	14.1	---	---	2.2	1.1
PSOC-623	---	---	0.2	0.2	1.2	---	0.1	0.2	---
PSOC-95	---	2.4	---	---	5.9	---	0.9	0.4	0.2
DJR-37 (POC-339)	---	2.0	---	---	25.7	---	2.5	---	---
DJR-39 (POC-340)	0.9	2.5	1.7	0.1	3.7	---	1.3	2.4	0.8

Table 3. (continued)

Sample	252A (17.24)	253 (17.59)	268 (18.31)	268 (18.86)	264 (19.02)	208 (19.03)	268 (19.14)	297 (19.61)	310A (20.52)
DJR-71 (PSOC-256)	5.3	0.7	2.4	---	---	---	---	1.6	7.4
DJR-67 (PSOC-330)	---	1.0	---	---	---	---	---	---	2.1
PSOC-349	5.1	1.3	---	---	22.4	---	---	---	0.8
PSOC-124	4.8	0.5	2.1	---	---	---	1.3	1.7	3.9
PSOC-372	3.5	0.8	5.1	---	---	42.7	---	0.8	3.4
PSOC-308	---	4.0	---	---	2.7	---	---	1.3	4.6
PSOC-641	---	3.1	11.0	4.1	---	---	2.4	1.4	3.9
DJR-47	4.5	---	2.3	3.4	---	---	---	---	2.2
DJR-44	3.2	0.6	2.8	4.7	---	---	---	---	1.5
PSOC-582	---	1.7	---	---	---	---	---	---	1.2
PSOC-399	---	4.2	---	---	1.1	---	---	0.9	3.6
DJR-69 (PSOC-405)	5.0	0.5	2.4	---	---	---	---	---	1.9
PSOC-155	1.9	---	---	---	---	82.4	---	---	2.2
PSOC-453	9.0	---	---	1.2	---	---	13.5	1.3	5.3
PSOC-459	6.4	---	1.5	3.6	---	---	25.8	1.8	3.0
PSOC-500	5.7	0.3	0.8	---	1.4	---	3.1	3.4	5.4
PSOC-503	5.0	1.2	4.0	---	4.5	---	---	2.8	6.7
DJR-66 (PSOC-312)	4.0	0.6	1.6	2.5	---	1.6	---	---	4.0
PSOC-450	2.5	3.2	4.2	6.0	6.2	---	---	7.1	7.8
DJR-70	---	1.3	---	---	---	---	---	---	1.2
DJR-20	8.2	1.5	1.9	2.9	---	---	1.8	---	4.0
PSOC-535	5.4	---	1.6	---	---	---	5.2	---	2.7
PSOC-418	---	1.5	3.1	---	---	---	---	---	5.2
PSOC-623	0.8	---	0.2	---	0.3	3.6	---	---	0.5
PSOC-95	---	2.1	5.3	---	---	---	---	2.6	6.9
DJR-37 (POC-339)	9.6	0.8	0.9	---	---	---	---	---	0.4
DJR-39 (POC-340)	3.6	1.5	1.8	---	---	---	---	---	4.2

Table 3. (continued)

Sample	311 (21.00)	310B (21.05)	322 (21.18)	308 (22.19)	326 (22.79)	328 (23.20)	308 (23.58)	368 (24.31)	254 (24.47)
DJR-71 (PSOC-256)	2.8	---	---	0.7	---	---	0.2	---	---
DJR-67 (PSOC-330)	1.5	---	---	0.5	---	---	---	---	---
PSOC-349	0.7	---	---	1.3	---	---	---	---	---
PSOC-124	---	0.2	---	0.6	---	---	---	---	---
PSOC-372	0.8	---	---	---	---	---	0.8	---	---
PSOC-308	3.6	---	2.7	---	1.8	---	---	---	---
PSOC-641	---	1.2	---	0.3	---	---	---	---	---
DJR-47	---	1.1	---	1.0	---	---	---	0.7	---
DJR-44	1.6	---	---	0.5	---	---	---	---	---
PSOC-582	8.1	---	---	---	---	---	---	0.4	---
PSOC-399	7.0	---	2.2	2.1	---	2.6	2.9	1.8	---
DJR-69 (PSOC-405)	1.2	---	---	---	---	0.7	4.4	---	---
PSOC-155	---	---	---	---	---	---	---	---	---
PSOC-453	---	1.4	---	0.3	---	---	0.8	3.2	---
PSOC-459	---	1.5	---	0.5	---	---	---	---	---
PSOC-500	---	1.9	---	1.4	1.6	---	---	---	---
PSOC-503	---	1.4	0.5	0.4	4.2	---	---	---	---
DJR-66 (PSOC-312)	---	1.3	---	0.3	---	---	2.0	0.2	---
PSOC-450	---	3.4	3.6	---	5.7	---	---	0.7	---
DJR-70	0.7	---	---	---	---	---	---	---	---
DJR-20	0.2	0.6	---	---	3.0	---	3.8	---	---
PSOC-535	---	0.9	---	0.8	---	---	---	1.3	---
PSOC-418	---	2.0	---	0.3	---	---	---	1.8	---
PSOC-623	---	---	---	0.2	---	44.6	---	---	30.6
PSOC-95	0.5	---	---	0.7	---	---	0.6	---	---
DJR-37 (POC-339)	0.1	---	---	---	---	---	---	---	---
DJR-39 (POC-340)	---	0.9	---	---	2.6	---	0.2	---	---

Table 3. (continued)

Sample	% Total GC Area
DJR-71 (PSOC-256)	93.0
DJR-67 (PSOC-330)	95.4
PSOC-349	89.3
PSOC-124	93.5
PSOC-372	92.7
PSOC-308	84.5
PSOC-641	96.0
DJR-47	99.5
DJR-44	95.4
PSOC-582	89.2
PSOC-399	82.5
DJR-69 (PSOC-405)	83.9
PSOC-155	99.4
PSOC-453	94.7
PSOC-459	86.2
PSOC-500	94.4
PSOC-503	93.4
DJR-66 (PSOC-312)	88.7
PSOC-450	82.8
DJR-70	91.1
DJR-20	99.2
PSOC-535	88.9
PSOC-418	92.8
PSOC-623	98.1
PSOC-95	89.7
DJR-37 (POC-339)	91.9
DJR-39 (POC-340)	79.6

were detected, averaging 25-30 compounds per sample. The most probable structures were determined and the results are reported in Table 4. The distribution of the 52 compounds is shown by relative percent of total GC area in Table 5.

The response to the detector in the gas chromatograms was calculated from the contributions to the effective carbon number given in Table 6. Using the internal standard, the absolute yields of the major products were calculated. The results are reported in Table 7.

3. Oxidation of Model Compounds

The procedure was the same as in the parent coal oxidations except for the addition of the model compound. The model was added to the PTFA/H_2SO_4 mixture slowly over a 20-minute period of time to better simulate the oxidation of a coal sample. Also, the second addition of H_2O_2 was found not to be necessary.

Nine models were chosen for oxidation by way of the above procedure ranging from aromatic to dihydroaromatic to purely aliphatic and then examined by the same GC/MS procedures used for the parent coal and SRC samples. The relative percent GC areas were calculated and compared to the major components from the parent coal oxidations and to the products from the solvent refined coal oxidations. The results are reported in Table 8.

Table 4. Structures of Solvent Refined Coal PTFA Oxidation Products

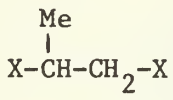
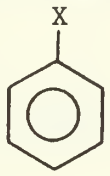
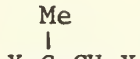
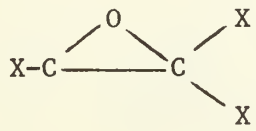
MW = 118 Ethanedioic Acid[a,b] X-X	MW = 160 2-Methylbutanedioic Acid 
MW = 132 Propanedioic Acid $X-CH_2-X$	MW = 136 Benzoic Acid 
MW = 144 cis-Butenedioic Acid X-CH=CH-X	MW = 158 cis-2-Methylbutenedioic Acid 
MW = 146 Butanedioic Acid $X-CH_2-CH_2-X$	MW = 160 Pentanedioic Acid $X-(CH_2)_3-X$
MW = 174 Hexanedioic Acid $X-(CH_2)_4-X$	MW = 218B Oxiranetricarboxylic Acid 

Table 4. (continued)

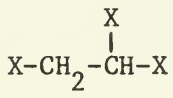
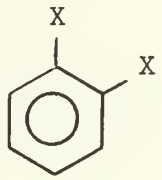
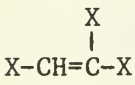
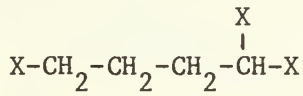
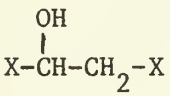
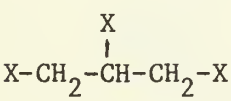
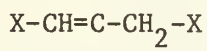
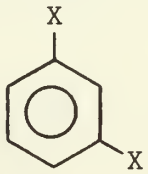
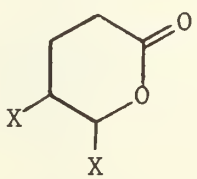
MW = 204 2-Carboxybutanedioic Acid 	MW = 194A Benzene-1,2-dicarboxylic Acid 
MW = 202A 2-Carboxybutenedioic Acid 	MW = 232 x-Carboxyhexanedioic Acid (two isomers) 
MW = 220 2-Hydroxybutanedioic Acid 	MW = 194B Benzene-1,4-dicarboxylic Acid 
MW = 218A 3-Carboxypentanedioic Acid 	MW = 216A 3-Carboxy-2-pentenedioic Acid 
MW = 194C Benzene-1,3-dicarboxylic Acid 	MW = 216B x,y-Dicarboxypentanolide (three isomers) 

Table 4. (continued)

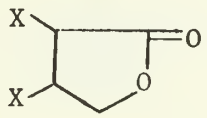
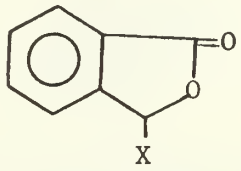
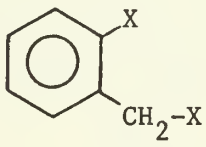
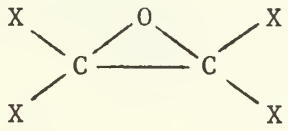
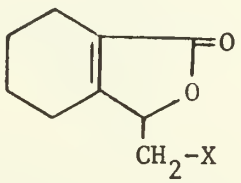
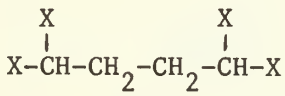
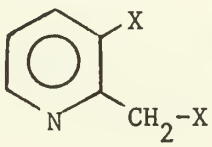
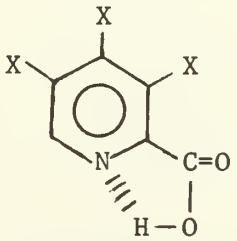
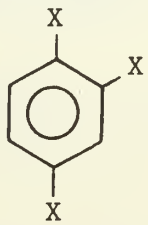
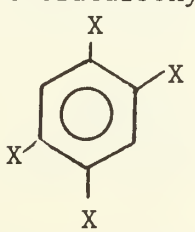
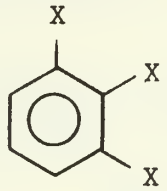
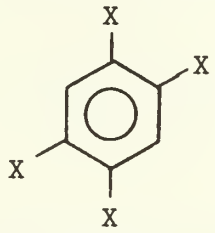
MW = 202B x,y-Dicarboxybutanolide 	MW = 192 Phthalide-3-carboxylic Acid 
MW = 208 2-Carboxybenzeneacetic Acid 	MW = 276 Oxiranetetracarboxylic Acid 
MW = 210 4,5,6,7-Tetrahydrophthalide-3-acetic Acid[c] 	MW = 290 x,y-Dicarboxyhexanedioic Acid (two isomers) 
MW = 209 3-Carboxypyridine-2-acetic Acid 	MW = 239 Pyridine-2,x,y-tricarboxylic Acid 
MW = 252A Benzene-1,2,4-tricarboxylic Acid 	MW = 297 Pyridine-2,x,y,z-tetracarboxylic Acid 

Table 4. (continued)

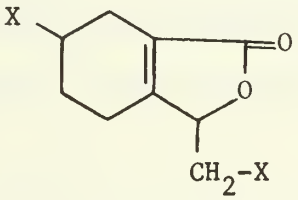
MW = 252B Benzene-1,2,3-tricarboxylic Acid



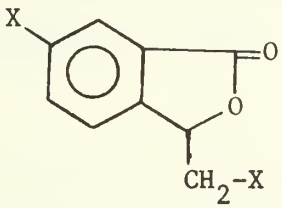
MW = 310A Benzene-1,2,4,5-tetracarboxylic Acid



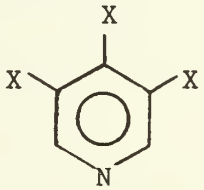
MW = 268 x-Carboxy-4,5,6,7-tetrahydrophthalide-3-acetic Acid (three isomers)



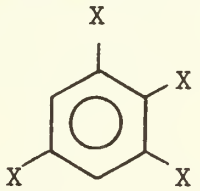
MW = 264 x-Carboxyphthalide-3-acetic Acid



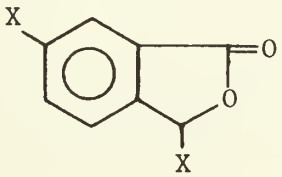
MW = 253 Pyridine-x,y,z-tricarboxylic Acid



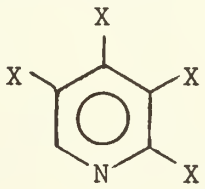
MW = 310B Benzene-1,2,3,5-tetracarboxylic Acid



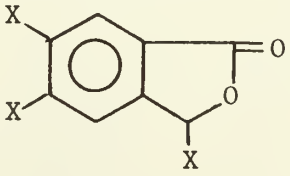
MW = 250 x-Carboxyphthalide-3-carboxylic Acid (four isomers)



MW = 311 Pyridine-2,x,y,z-tetracarboxylic Acid



MW = 308 x,y-Dicarboxyphthalide-3-carboxylic Acid (two isomers)



MW = 368 Benzene-1,2,3,4,5-pentacarboxylic Acid

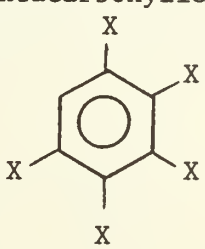
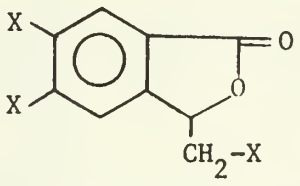


Table 4. (continued)

MW = 322 x,y-Dicarboxyphthalide-3-acetic Acid 	

[a]X = CO_2Me.

[b]All products are named for the corresponding acid.

[c]Phthalide = 1(3H)-isobenzo-furanone.

Table 5. PTFA Oxidations of Solvent Refined Coals

Coal	Sample	Relationship	118 (2.09)	132 (3.20)	144 (4.31)	146 (4.60)	160 (4.90)	136 (5.15)	158 (5.87)
PSOC-256	DJR-80	Parent	6.4	31.4	0.4	9.3	---	---	0.7
	DJ-SRC-1D	Short Time SRC	---	6.6	0.4	8.4	---	13.1	2.1
	DJ-SRC-6D	Long Time SRC	---	4.4	---	8.9	---	11.4	1.4
	DJ-SRC-11D	Residue	7.6	17.7	---	6.2	---	7.4	0.9
PSOC-312	DJR-83	Parent	---	19.6	---	9.7	---	---	---
	DJ-SRC-2D	Short Time SRC	---	5.2	---	14.0	6.3	10.6	4.0
	DJ-SRC-7D	Long Time SRC	---	10.2	---	17.5	---	9.7	0.6
	DJ-SRC-12D	Residue	2.9	23.5	---	7.5	---	5.8	0.6
PSOC-330	DJR-77	Parent	9.1	31.5	2.4	12.9	---	---	0.5
	DJ-SRC-3D	Short Time SRC	---	17.9	0.7	9.3	---	13.6	3.0
	DJ-SRC-8D	Long Time SRC	---	2.2	1.0	9.1	---	11.0	2.3
	DJ-SRC-13D	Residue	23.2	10.1	2.5	11.7	---	6.7	3.0
PSOC-372	DJR-79	Parent	2.5	26.9	1.3	10.3	2.6	---	0.4
	DJ-SRC-4D	Short Time SRC	---	19.6	---	9.6	4.0	9.6	1.8
	DJ-SRC-9D	Long Time SRC	---	11.5	0.6	8.0	5.9	6.7	3.1
	DJ-SRC-14D	Residue	4.7	18.4	1.1	2.5	2.8	3.4	1.9
SPCO-405	DJR-84	Parent	0.6	19.3	5.5	8.2	---	---	1.9
	DJ-SRC-5D	Short Time SRC	---	3.4	0.8	13.6	---	12.6	2.8
	DJ-SRC-10E	Long Time SRC	---	0.8	---	11.3	---	10.7	1.2
	DJ-SRC-15D	Residue	4.4	9.4	0.4	4.8	---	4.8	0.7

Table 5. (continued)

Sample	160 (6.45)	174 (8.22)	204 (9.23)	202 (9.90)	220 (10.51)	218 (10.54)	218 (10.97)	194 (11.14)	232 (11.17)	194 (11.33)
DJR-80	---	---	3.2	0.7	---	2.1	3.3	0.8	---	1.9
DJ-SRC-1D	---	---	0.1	0.3	---	1.7	0.7	4.3	---	4.0
DJ-SRC-6D	---	---	0.5	0.3	0.5	1.5	8.5	5.4	---	5.5
DJ-SRC-11D	---	---	2.5	---	---	0.5	3.8	5.4	---	2.6
DJR-83	0.5	---	4.8	0.7	4.7	5.2	16.7	---	4.6	---
DJ-SRC-2D	5.4	2.4	2.2	0.3	0.7	1.3	8.9	---	7.6	5.6
DJ-SRC-7D	2.9	0.1	0.4	---	---	3.3	6.0	---	3.3	5.1
DJ-SRC-12D	---	0.3	3.2	---	---	2.1	8.5	2.3	---	1.7
DJR-77	1.4	0.7	3.2	0.3	---	2.9	3.8	---	0.9	0.8
DJ-SRC-3D	1.0	---	1.6	0.4	0.8	0.8	10.7	---	5.2	5.0
DJ-SRC-8D	---	---	0.2	---	---	1.4	2.9	5.4	---	8.5
DJ-SRC-13D	---	0.3	0.4	0.2	---	1.2	1.3	2.1	---	1.8
DJR-79	0.3	---	3.4	0.4	0.4	2.2	7.3	---	3.4	---
DJ-SRC-4D	1.1	---	1.4	0.6	1.1	0.9	11.5	---	2.6	3.7
DJ-SRC-9D	1.6	---	0.6	0.1	0.6	0.9	6.7	---	8.9	4.4
DJ-SRC-14D	1.8	1.8	1.0	0.6	---	3.8	4.2	5.2	---	2.9
DJR-84	0.6	---	2.2	0.5	1.4	0.8	6.7	6.8	---	4.8
DJ-SRC-5D	0.8	---	0.3	---	---	2.9	5.4	6.0	---	7.5
DJ-SRC-10E	1.2	---	0.5	---	---	3.4	1.8	7.8	---	11.8
DJ-SRC-15D	---	---	0.3	---	---	0.8	2.6	4.7	---	3.1

Table 5. (continued)

Sample	216 (11.54)	194 (11.58)	232 (11.88)	202 (11.98)	250 (12.24)	208 (12.60)	210 (12.72)	209 (13.14)	216 (13.11)
DJR-80	---	1.6	---	0.5	---	---	2.5	---	---
DJ-SRC-1D	---	4.2	---	0.8	---	---	2.4	---	---
DJ-SRC-6D	---	3.8	---	0.4	1.3	0.6	0.8	0.4	---
DJ-SRC-11D	---	1.9	---	---	---	---	1.8	---	---
DJR-83	---	1.5	---	0.9	2.0	---	1.3	---	0.9
DJ-SRC-2D	1.5	---	0.6	1.3	---	---	3.2	---	---
DJ-SRC-7D	---	6.0	---	0.6	0.5	---	0.6	0.5	---
DJ-SRC-12D	---	2.5	---	0.6	---	---	1.6	0.7	---
DJR-77	---	0.6	---	1.1	---	---	2.7	---	---
DJ-SRC-3D	---	---	---	2.0	---	0.6	1.4	---	---
DJ-SRC-8D	---	6.4	---	0.5	---	---	1.5	0.6	---
DJ-SRC-13D	---	1.6	1.2	---	---	---	2.1	---	---
DJR-79	1.8	---	---	1.0	---	---	2.8	---	0.9
DJ-SRC-4D	---	2.8	---	0.7	---	0.4	1.2	0.7	---
DJ-SRC-9D	---	2.4	---	0.4	---	2.3	1.3	0.5	---
DJ-SRC-14D	---	2.4	---	0.8	---	---	2.5	0.7	---
DJR-84	---	2.5	---	1.2	---	4.2	1.2	---	---
DJ-SRC-5D	---	5.6	---	0.5	---	---	0.6	---	---
DJ-SRC-10E	---	---	---	1.3	---	---	2.9	1.1	---
DJ-SRC-15D	---	3.4	---	0.6	---	---	2.6	0.7	---

Table 5. (continued)

Sample	216 (13.24)	216 (13.75)	192 (13.79)	276 (14.33)	290 (14.92)	290 (15.20)	239 (15.54)	252 (15.79)	252 (16.14)
DJR-80	0.9	0.4	---	2.0	---	---	0.3	11.2	---
DJ-SRC-1D	0.4	0.5	---	3.6	0.4	---	0.5	19.3	0.5
DJ-SRC-6D	---	---	0.5	3.7	---	1.4	---	18.9	0.2
DJ-SRC-11D	---	---	---	3.1	---	---	0.4	21.0	---
DJR-83	0.5	0.7	---	5.5	0.7	1.1	---	7.3	0.6
DJ-SRC-2D	---	---	0.7	2.7	---	0.9	---	6.4	2.2
DJ-SRC-7D	---	---	0.6	4.0	---	0.2	---	15.2	0.1
DJ-SRC-12D	---	---	---	3.5	---	---	0.3	10.9	0.5
DJR-77	0.7	0.3	---	3.1	---	0.2	0.2	4.9	---
DJ-SRC-3D	0.4	---	0.4	3.5	---	0.4	---	12.3	---
DJ-SRC-8D	---	---	0.5	3.8	---	---	0.4	17.9	0.1
DJ-SRC-13D	---	---	---	1.6	---	---	0.6	9.2	---
DJR-79	---	0.3	---	2.8	0.3	0.3	---	10.6	---
DJ-SRC-4D	---	---	0.7	3.9	---	0.6	---	7.9	3.0
DJ-SRC-9D	---	---	1.4	2.4	---	1.1	---	11.9	4.2
DJ-SRC-14D	---	0.5	---	0.7	---	---	1.8	14.4	---
DJR-84	---	0.5	---	2.7	---	0.7	---	12.6	0.8
DJ-SRC-5D	---	---	0.3	3.5	---	0.3	0.8	14.3	0.5
DJ-SRC-10E	---	---	1.6	4.5	---	0.4	0.6	17.0	1.4
DJ-SRC-15D	---	0.6	---	4.4	---	---	1.1	18.2	---

Table 5. (continued)

Sample	268 (16.61)	253 (16.77)	268 (17.08)	250 (17.19)	250 (17.80)	250 (17.96)	268 (18.11)	297 (18.30)	250 (18.67)
DJR-80	1.6	0.9	5.5	---	---	---	1.6	1.2	0.8
DJ-SRC-1D	2.2	---	3.7	1.5	0.7	0.2	---	1.5	1.4
DJ-SRC-6D	1.9	---	1.9	0.8	0.6	0.8	---	---	0.4
DJ-SRC-11D	1.5	---	3.3	---	---	---	1.2	0.6	---
DJR-83	0.6	---	2.7	---	---	---	0.7	0.6	0.2
DJ-SRC-2D	0.5	---	0.7	0.8	1.2	0.6	---	---	0.3
DJ-SRC-7D	0.5	---	1.6	0.8	0.4	0.7	---	---	0.4
DJ-SRC-12D	0.6	---	3.7	---	0.5	---	1.0	1.4	---
DJR-77	1.2	0.4	4.4	---	---	---	1.1	0.8	---
DJ-SRC-3D	0.4	---	2.1	0.3	0.3	0.5	---	---	---
DJ-SRC-8D	1.1	---	2.8	0.9	0.9	0.5	---	2.1	1.4
DJ-SRC-13D	0.5	---	1.7	---	---	0.6	0.9	---	2.2
DJR-79	1.4	1.0	3.8	---	---	---	1.3	0.8	0.3
DJ-SRC-4D	0.9	---	2.7	---	0.8	0.7	---	0.9	---
DJ-SRC-9D	1.3	---	1.8	0.9	0.9	1.2	---	---	0.2
DJ-SRC-14D	1.4	---	2.7	---	0.6	---	0.9	1.1	---
DJR-84	1.1	---	2.3	0.9	0.7	---	---	1.2	0.2
DJ-SRC-5D	0.6	---	0.7	0.7	0.4	---	---	2.2	1.2
DJ-SRC-10E	1.0	---	1.2	1.6	0.4	0.5	---	3.9	2.1
DJ-SRC-15D	3.1	---	5.4	---	1.6	---	1.9	3.4	---

Table 5. (continued)

Sample	310 (19.18)	264 (19.32)	310 (19.50)	311 (20.19)	308 (20.54)	308 (21.05)	322 (21.44)	368 (21.75)
DJR-80	7.4	---	---	0.5	0.4	0.9	---	---
DJ-SRC-1D	10.2	---	1.5	---	0.5	1.5	---	1.0
DJ-SRC-6D	8.2	---	1.6	---	1.9	1.5	---	0.3
DJ-SRC-11D	8.3	---	1.4	---	0.7	---	---	---
DJR-83	3.2	---	0.7	---	0.9	1.0	---	---
DJ-SRC-2D	1.5	---	0.3	---	0.5	---	---	---
DJ-SRC-7D	5.0	0.4	0.7	---	1.1	0.6	0.4	---
DJ-SRC-12D	7.4	---	1.6	---	---	1.2	---	---
DJR-77	4.7	---	---	1.3	0.9	1.1	---	---
DJ-SRC-3D	3.3	---	0.4	---	1.0	0.5	---	0.4
DJ-SRC-8D	8.0	0.7	1.8	---	1.2	1.8	0.9	0.3
DJ-SRC-13D	7.4	---	2.7	---	---	2.9	---	---
DJR-79	6.3	---	---	0.9	1.1	0.9	---	---
DJ-SRC-4D	3.4	---	0.3	---	1.0	0.1	---	---
DJ-SRC-9D	4.1	---	0.6	---	1.1	0.5	---	---
DJ-SRC-14D	8.2	---	1.5	---	---	---	---	---
DJR-84	5.1	---	1.1	---	1.3	0.5	---	---
DJ-SRC-5D	8.5	0.4	1.1	---	0.7	0.4	0.3	0.6
DJ-SRC-10E	5.1	---	0.8	---	0.3	0.4	0.8	0.7
DJ-SRC-15D	10.6	---	1.9	---	---	0.7	---	1.2

Table 6. Contributions to Effective Carbon Number[a]

Atom	Type	Effective Carbon Number Contribution
Carbon	Aliphatic	1.0
Carbon	Aromatic	1.0
Carbon	Olefinic	0.95
Carbon	Acetylenic	1.3
Carbon	Carbonyl	0.0
Carbon	Nitrile	0.3
Oxygen	Ether	-1.0
Oxygen	Primary alcohol	-0.6
Oxygen	Secondary alcohol	-0.75
Oxygen	Tertiary alcohol, esters	-0.25
Chlorine	Two or more on single aliphatic C	-0.12 each
Chlorine	On olifinic C	0.05
Nitrogen	In Amines	Similar to O in corresponding alcohols

[a]R. L. Grob, "Modern Practive of Gas Chromatography," John Wiley and Sons, New York, 1977, p. 254.

Table 7. Absolute Yields (mg/gr sample) of PTFA Oxidations of Solvent Refined Coals

Coal	Sample	Relationship	132	146	136	204	218	218	194	194	194	276
PSOC-256	DJR-80	Parent	18.7	3.9	---	1.1	0.6	1.8	0.2	0.5	0.4	0.9
	DJ-SRC-1D	Short Time SRC	6.8	6.2	5.9	0.1	0.8	0.7	2.0	1.9	1.9	2.7
	DJ-SRC-6D	Long Time SRC	5.8	8.4	6.6	0.4	1.0	10.2	3.2	3.3	2.3	3.5
	DJ-SRC-11D	Residue	12.5	3.1	2.3	1.0	0.2	2.4	1.7	0.8	0.6	1.6
PSOC-312	DJR-83	Parent	13.8	4.9	---	2.0	1.8	10.7	---	---	0.5	2.8
	DJ-SRC-2D	Short Time SRC	6.7	12.8	5.9	1.6	0.8	10.4	---	3.3	---	2.5
	DJ-SRC-7D	Long Time SRC	11.7	14.3	4.8	0.3	1.8	6.2	---	2.6	3.1	3.3
	DJ-SRC-12D	Residue	14.8	3.4	1.6	1.2	0.6	4.9	0.7	0.5	0.7	1.6
PSOC-330	DJR-77	Parent	21.0	6.1	---	1.2	0.9	2.3	---	0.3	0.2	1.5
	DJ-SRC-3D	Short Time SRC	18.4	6.8	6.1	1.0	0.4	10.0	---	2.4	---	2.6
	DJ-SRC-8D	Long Time SRC	2.5	7.1	7.1	0.1	0.7	2.9	2.7	4.2	3.2	3.0
	DJ-SRC-13D	Residue	5.1	4.2	1.5	0.1	0.3	0.6	0.5	0.4	0.4	0.6
PSOC-372	DJR-79	Parent	17.7	4.9	---	1.2	0.7	4.3	---	---	---	1.3
	DJ-SRC-4D	Short Time SRC	10.5	3.7	2.3	0.5	0.2	5.6	---	0.9	0.7	1.5
	DJ-SRC-9D	Long Time SRC	13.7	6.8	3.5	0.4	0.5	7.2	---	2.4	1.3	2.0
	DJ-SRC-14D	Residue	7.8	0.7	0.6	0.3	0.7	1.6	1.0	0.4	0.5	0.2
PSOC-405	DJR-84	Parent	7.9	2.4	---	0.6	0.1	2.5	1.3	0.9	0.5	0.8
	DJ-SRC-5D	Short Time SRC	3.5	10.2	5.8	0.2	1.4	5.2	2.8	3.6	2.7	2.6
	DJ-SRC-10E	Long Time SRC	0.9	9.1	5.3	0.3	1.8	1.9	4.0	6.1	---	3.6
	DJ-SRC-15D	Residue	10.9	3.9	2.4	0.2	0.5	2.8	2.5	1.6	1.8	3.6

Table 7. (continued)

Sample	252	252	310	310
DJR-80	3.2	---	2.2	---
DJ-SRC-1D	9.3	0.3	5.3	0.8
DJ-SRC-6D	12.0	0.1	0.6	1.1
DJ-SRC-11D	7.0	---	2.9	0.5
DJR-83	2.5	0.2	1.1	0.2
DJ-SRC-2D	3.9	1.3	0.9	0.2
DJ-SRC-7D	8.2	0.1	2.8	0.4
DJ-SRC-12D	3.3	0.2	2.3	0.5
DJR-77	1.5	---	1.6	---
DJ-SRC-3D	6.0	---	1.7	0.2
DJ-SRC-8D	9.3	0.1	4.4	1.0
DJ-SRC-13D	2.2	---	1.9	0.7
DJR-79	3.3	---	2.1	---
DJ-SRC-4D	2.0	0.8	0.9	0.1
DJ-SRC-9D	6.7	2.4	2.4	0.4
DJ-SRC-14D	2.8	---	1.7	0.3
DJR-84	2.5	0.2	1.0	0.2
DJ-SRC-5D	7.2	0.2	4.5	0.6
DJ-SRC-10E	9.1	0.8	2.9	0.4
DJ-SRC-15D	10.0	---	6.1	1.1

Table 8. PTFA Oxidation Products of Models Versus Parent Coal and Solvent Refined Coal Products

PTFA Oxidations of Models Versus Parent Coals

Sample	132	144	146	160	176	160	162	174	188	204	202
Pyrene	---	---	---	---	---	---	---	---	---	0.2	---
Perylene	---	---	2.4	---	---	---	---	---	---	---	0.2
Fluoranthrene	---	---	---	---	---	---	---	---	---	---	---
Decalin	0.6	---	42.2	---	---	28.1	---	11.9	---	---	---
9,10-Dihydroanthracene	9.7	0.8	8.0	---	---	---	---	---	---	0.2	---
5,12-Dihydronaphthacene	---	0.1	1.5	---	---	0.8	---	---	---	---	---
5,12-Dihydro-benz(a)-anthracene	16.5	1.0	8.9	---	---	0.1	4.2	---	---	2.5	0.4
7,14-Dihydro-dibenz(a,h)-anthracene	1.0	0.6	4.3	---	---	1.0	---	---	---	---	---
Maleic anhydride-anthracene adduct	1.9	2.6	5.9	---	0.2	---	---	---	---	0.5	---

PTFA Oxidations of Models Versus Solvent Refined Coals

Sample	132	144	146	160	136	158	160	174	204	202	220
Pyrene	---	---	---	---	---	---	---	---	0.2	---	---
Perylene	---	---	2.4	---	0.9	---	---	---	---	0.2	---
Fluoranthrene	---	---	---	---	---	---	---	---	---	---	---
Decalin	0.6	---	42.2	---	---	---	28.1	11.9	---	---	---
9,10-Dihydroanthracene	9.7	0.8	8.0	---	3.9	---	---	---	0.2	---	---
5,12-Dihydronaphthacene	---	0.1	1.5	---	1.4	---	0.8	---	---	---	---
5,12-Dihydro-benz(a)-anthracene	16.5	1.0	8.9	---	5.2	---	0.4	---	2.5	0.4	1.1
7,14-Dihydro-dibenz(a,h)-anthracene	1.0	0.6	4.3	---	9.1	2.8	1.0	---	---	---	---
Maleic anhydride-anthracene adduct	1.9	2.6	5.9	---	1.3	---	---	---	0.5	---	0.3

Table 8. (continued)

PTFA Oxidations of Models Versus Parent Coals

Sample	220	218	218	194	232	234	194	195	216	232	202
Pyrene	---	0.5	1.6	1.6	---	---	---	---	---	---	---
Perylene	---	1.7	0.7	9.8	---	---	---	---	---	---	---
Fluoranthrene	---	5.0	2.6	16.2	---	---	---	---	---	---	---
Decalin	---	---	---	---	---	---	---	---	---	---	---
9,10-Dihydroanthracene	---	1.5	1.2	28.0	---	---	---	---	---	---	0.5
5,12-Dihydronaphthacene	---	1.9	3.9	20.3	---	---	1.9	---	---	---	---
5,12-Dihydro-benz(a)-anthracene	1.1	1.2	3.0	35.7	---	0.9	---	---	---	---	---
7,14-Dihydro-dibenz(a,h)-anthracene	---	0.1	5.1	19.3	---	---	---	---	---	---	---
Maleic anhydride-anthracene adduct	0.3	2.9	6.0	6.3	0.9	---	---	---	---	---	0.5

PTFA Oxidations of Models Versus Solvent Refined Coals

Sample	218	218	194	232	194	216	194	232	202	250	208
Pyrene	0.5	1.6	1.6	---	3.6	---	11.1	---	---	---	---
Perylene	1.7	0.7	9.8	---	---	---	33.1	---	---	---	---
Fluoranthrene	5.0	2.6	16.2	---	---	---	20.2	---	---	---	---
Decalin	---	---	---	---	---	---	---	1.4	---	---	---
9,10-Dihydroanthracene	1.5	1.2	28.0	---	---	---	---	---	0.5	---	---
5,12-Dihydronaphthacene	1.9	3.9	20.3	---	1.9	---	---	---	---	---	---
5,12-Dihydro-benz(a)-anthracene	1.2	3.0	35.7	---	---	---	---	---	---	---	---
7,14-Dihydro-dibenz(a,h)-anthracene	0.1	5.0	19.3	---	---	---	8.5	---	---	---	---
Maleic anhydride-anthracene adduct	2.9	6.0	6.3	0.9	---	---	---	---	0.5	---	---

Table 8. (continued)

PTFA Oxidations of Models Versus Parent Coals

Sample	194	202	195	210	232	216	216	276	276	239	290
Pyrene	11.1	---	---	6.9	---	---	---	0.7	---	---	---
Perylene	33.1	---	---	6.9	---	---	---	1.7	---	---	---
Fluoranthrene	20.2	---	---	5.5	---	---	---	---	0.4	---	---
Decalin	---	---	---	---	1.4	---	---	---	---	---	---
9,10-Dihydroanthracene	---	---	---	---	---	---	---	---	1.3	---	---
5,12-Dihydronaphthacene	---	---	---	---	---	---	---	---	0.7	---	---
5,12-Dihydro-benz(a)-anthracene	---	---	---	0.5	---	---	---	---	---	---	---
7,14-Dihydro-dibenz(a,h)-anthracene	8.5	---	---	0.4	---	---	---	1.4	---	---	---
Maleic anhydride-anthracene adduct	---	---	---	---	---	0.2	---	---	1.2	---	3.9

PTFA Oxidations of Models Versus Solvent Refined Coals

Sample	210	209	216	216	216	192	276	290	290	239	252
Pyrene	2.1	---	---	---	---	0.9	---	---	---	---	13.5
Perylene	0.3	---	---	---	---	1.5	---	---	---	---	9.3
Fluoranthrene	---	---	---	---	---	2.6	0.4	---	---	---	6.4
Decalin	---	---	---	---	---	---	---	---	---	---	---
9,10-Dihydroanthracene	---	---	---	---	---	4.4	1.3	---	---	---	0.7
5,12-Dihydronaphthacene	---	---	---	---	---	0.8	0.7	---	---	---	19.3
5,12-Dihydro-benz(a)-anthracene	0.5	---	---	---	---	3.9	---	---	---	---	---
7,14-Dihydro-dibenz(a,h)-anthracene	0.4	---	---	---	---	0.5	---	---	---	---	9.4
Maleic anhydride-anthracene adduct	---	---	---	0.2	---	2.6	1.3	3.9	1.5	---	9.1

Table 8. (continued)

PTFA Oxidations of Models Versus Parent Coals

Sample	290	274	252	253	268	268	264	208	268	297	310
Pyrene	---	---	13.5	---	---	---	0.5	---	---	---	---
Perylene	---	---	9.3	---	---	---	11.7	---	---	---	---
Fluoranthrene	---	---	6.4	---	---	---	3.2	---	---	---	---
Decalin	---	---	---	---	---	---	---	---	---	---	---
9,10-Dihydroanthracene	---	---	0.7	---	---	---	0.5	12.9	---	---	0.9
5,12-Dihydronaphthacene	---	---	19.3	---	1.6	---	---	---	---	---	28.6
5,12-Dihydro-benz(a)-anthracene	---	---	---	---	---	1.0	0.8	---	---	---	---
7,14-Dihydro-dibenz(a,h)-anthracene	---	---	9.4	---	---	---	---	---	---	---	2.2
Maleic anhydride-anthracene adduct	1.5	---	9.1	---	0.5	0.5	---	---	---	---	20.6

PTFA Oxidations of Models Versus Solvent Refined Coals

Sample	252	268	253	268	250	250	250	268	297	250	310
Pyrene	---	---	---	---	7.7	1.3	---	---	---	7.2	---
Perylene	3.6	---	---	---	5.3	---	---	---	---	---	---
Fluoranthrene	4.7	---	---	---	5.4	---	0.5	---	---	---	---
Decalin	---	---	---	---	---	---	---	---	---	---	---
9,10-Dihydroanthracene	---	---	---	---	---	---	---	---	---	---	0.9
5,12-Dihydronaphthacene	0.8	1.6	---	---	---	---	---	---	---	---	28.6
5,12-Dihydro-benz(a)-anthracene	---	---	---	1.0	---	---	---	---	---	---	---
7,14-Dihydro-dibenz(a,h)-anthracene	---	---	---	---	4.9	2.1	---	---	---	---	2.2
Maleic anhydride-anthracene adduct	0.3	0.5	---	0.5	---	---	---	---	---	---	20.6

Table 8. (continued)

PTFA Oxidations of Models Versus Parent Coals

Sample	311	310	322	308	326	328	308	368	254	% Total GC Area
Pyrene	---	---	3.0	3.3	---	---	6.1	---	---	52.6
Perylene	---	---	1.1	1.4	---	---	0.7	---	0.5	81.1
Fluoranthrene	---	---	0.6	---	---	---	---	---	14.6	74.5
Decalin	---	---	---	---	---	---	---	---	---	84.1
9,10-Dihydroanthracene	---	---	---	---	---	---	---	---	---	66.8
5,12-Dihydronaphthacene	---	1.4	1.1	---	---	---	---	---	---	83.1
5,12-Dihydro-benz(a)-anthracene	---	---	---	---	---	---	---	---	---	78.1
7,14-Dihydro-dibenz(a,h)-anthracene	---	0.4	1.4	2.1	---	---	2.8	---	---	59.9
Maleic anhydride-anthracene adduct	---	2.5	---	---	---	1.1	0.7	---	---	69.6

PTFA Oxidations of Models Versus Solvent Refined Coals

Sample	264	310	311	308	308	322	368	% Total GC Area
Pyrene	0.5	---	---	3.3	6.1	12.3	---	73.3
Perylene	11.7	---	---	1.4	0.7	1.1	---	83.5
Fluoranthrene	3.2	---	---	---	---	0.6	---	67.8
Decalin	---	---	---	---	---	---	---	84.1
9,10-Dihydroanthracene	1.1	---	---	---	---	---	---	62.1
5,12-Dihydronaphthacene	---	1.4	---	---	---	1.1	---	86.1
5,12-Dihydro-benz(a)-anthracene	0.8	---	---	---	---	---	---	82.1
7,14-Dihydro-dibenz(a,h)-anthracene	---	0.4	---	2.1	2.2	3.6	---	80.1
Maleic anhydride-anthracene adduct	---	2.5	---	---	0.7	---	---	72.6

D. Nitric Acid Oxidations

A 0.5 g sample of the coal (-20 mesh) was stirred with 30 ml of 40% aqueous nitric acid at 60°C for five hours. The volatile material was removed on a rotary evaporator at 100°C and 2 PKa. The residue was converted to the methyl esters with BF_3 in methanol as in the PTFA oxidations. A CH_2Cl_2 solution of the esters was wahsed with saturated aqueous NaCl, saturated $NaCl/NaHCO_3$ solutions and then dried over $MgSO_4$. The solution was decanted and the excess CH_2Cl_2 was removed on a rotary evaporator.

Six parent coal samples were oxidized using the above procedure and analyzed by gas chromatography and mass spectrometry as before. Thirty-two compounds were detected, averaging 20-25 compounds per sample. The most probable structures of these compounds were determined and are reported in Table 9. The relative percent of the total GC peak areas were determined and the distribution of these is reported in Table 10.

Table 9. Structures of Parent Coals HNO_3 Oxidation Products

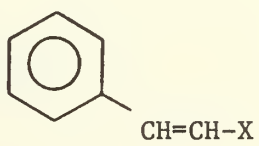
MW = 146 Butanedioic Acid[a,b] $X\text{-}(CH_2)_2\text{-}X$	MW = 174 Hexanedioic Acid $X\text{-}(CH_2)_4\text{-}X$
MW = 160 2-Methylbutanedioic Acid $X\text{-}CH(Me)\text{-}CH_2\text{-}X$	MW = 188 x-Methylhexanedioic Acid $X\text{-}CH(Me)\text{-}(CH_2)_3\text{-}X$
MW = 160 Pentanedioic Acid $X\text{-}(CH_2)_3\text{-}X$	MW = 188 Heptanedioic Acid $X\text{-}(CH_2)_5\text{-}X$
MW = 174 x-Methylpentanedioic $X\text{-}CH(Me)\text{-}(CH_2)_2\text{-}X$	MW = 162 Benzenepropenoic Acid 
MW = 202 Octanedioic Acid $X\text{-}(CH_2)_6\text{-}X$	MW = 232 x-Carboxyhexanedioic Acid $X\text{-}(CH_2)_3\text{-}CH(X)\text{-}X$

Table 9. (continued)

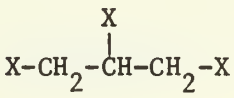
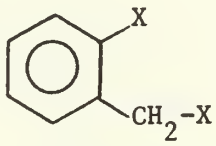
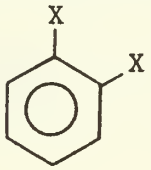
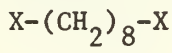
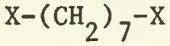
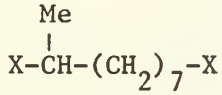
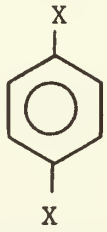
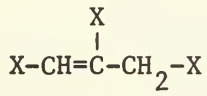
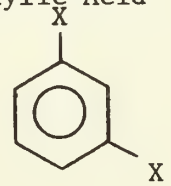
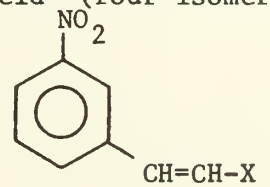
MW = 218 3-Carboxypentanedioic Acid 	MW = 208 2-Carboxybenzeneacetic Acid 
MW = 194A Benzene-1,2-dicarboxylic Acid 	MW = 230 Decanedioic Acid 
MW = 216 Nonanedioic Acid 	MW = 244 x-Methyldecanedioic Acid 
MW = 194B Benzene-1,4-dicarboxylic Acid 	MW = 216 3-Carboxy-2-pentenedioic Acid 
MW = 194C Benzene-1,3-dicarboxylic Acid 	MW = 207 3-Nitrobenzenepropenoic Acid (four isomers) 

Table 9. (continued)

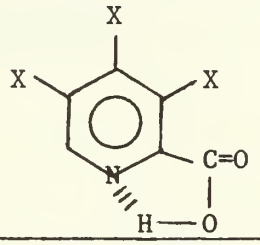
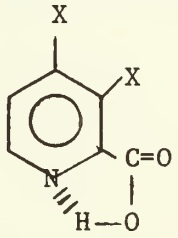
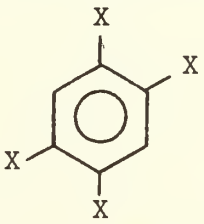
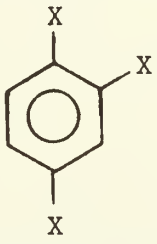
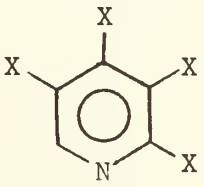
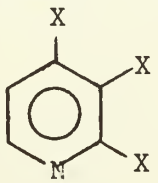
MW = 244 Undecanedioic Acid $X-(CH_2)_9-X$	MW = 297 Pyridine-2,x,y,z-tetracarboxylic Acid 
MW = 258 Dodecanedioic Acid $X-(CH_2)_{10}-X$	MW = 300 Pentadecanedioic Acid $X-(CH_2)_{13}-X$
MW = 239 Pyridine-2,x,y-tricarboxylic Acid 	MW = 310 Benzene-1,2,4,5-tetracarboxylic Acid 
MW = 252 Benzene-1,2,4-tricarboxylic Acid 	MW = 311 Pyridine-2,x,y,z-tetracarboxylic Acid 
MW = 253 Pyridine-x,y,z-tricarboxylic Acid 	

Table 9. (continued)

[a]X = CO_2Me.

[b]All products are named for the corresponding acid.

Table 10. HNO_3 Oxidations of Parent Coals

Province	Sample	State	Name	146 (4.85)	160 (5.17)	160 (6.17)	174 (6.63)	174 (7.68)
Eastern	PSOC-124	WV	WV Lower Kittaning	8.3	---	15.6	---	17.4
Interior	DJR-47	IL	IL #6 Monterey	4.6	5.0	6.1	6.8	7.7
Rocky Mountain	PSOC-155	UT	UT Mesa Verde	10.5	---	14.9	---	17.3
Interior	DJR-69 (PSOC-405)	OK	OK Lower Hartshorng	6.6	0.7	0.5	0.7	2.9
Great Plains	DJR-29	WY	Wyodak	3.3	1.7	5.1	2.0	5.6
Eastern	PSOC-110	PA	Pittsburg Seam	3.4	2.1	5.0	2.2	5.3

Table 10. (continued)

Sample	188 (7.99)	188 (9.02)	162 (9.68)	202 (10.31)	218 (10.50)	194 (11.15)	216 (11.43)	194 (11.49)	194 (11.89)
PSOC-124	---	15.9	---	13.0	---	2.7	9.4	---	---
DJR-47	---	5.2	---	4.3	4.8	7.9	5.0	---	---
PSOC-155	---	18.0	---	13.5	---	2.0	9.9	---	---
DJR-69 (PSOC-405)	---	1.9	---	2.8	0.9	26.0	---	6.3	3.5
DJR-29	2.4	6.3	8.4	4.7	3.1	1.2	4.0	---	---
PSOC-110	---	4.8	---	3.5	2.3	15.3	3.6	6.1	---

Table 10. (continued)

Sample	232 (11.92)	208 (12.49)	230 (12.66)	244 (13.10)	216 (13.12)	207 (13.38)	244 (13.74)	207 (14.84)	258 (14.90)
PSOC-124	---	---	6.2	---	---	---	3.0	---	7.7
DJR-47	2.5	---	5.2	3.3	---	---	1.4	---	3.7
PSOC-155	---	---	5.2	---	---	---	2.0	---	5.7
DJR-69 (PSOC-405)	---	20.7	---	---	---	---	1.7	---	1.8
DJR-29	1.8	---	2.9	---	1.6	2.0	1.9	20.6	1.3
PSOC-110	1.6	5.2	---	1.4	---	---	0.6	---	---

Table 10. (continued)

Sample	239 (14.98)	207 (15.33)	207 (15.61)	252 (15.73)	253 (15.98)	297 (16.71)	300 (17.44)	310 (18.96)	311 (19.78)
PSOC-124	---	---	---	---	---	---	---	---	---
DJR-47	3.9	---	---	11.0	---	1.5	3.6	6.4	3.6
PSOC-155	---	---	---	---	---	---	---	---	---
DJR-69 (PSOC-405)	5.3	---	---	10.0	3.6	---	2.8	4.5	2.8
DJR-29	---	1.2	12.5	4.0	---	---	1.1	1.4	---
PSOC-110	4.3	---	---	16.1	2.5	2.1	2.8	8.0	2.8

Table 10. (continued)

Sample	% Total GC Area
PSOC-124	99.3
DJR-47	100.0
PSOC-155	99.0
DJR-69 (PSOC-405)	100.0
DJR-29	100.0
PSOC-110	100.0

IV. DISCUSSION OF RESULTS

The original impetus for the research in this thesis came from previous work in our laboratory that showed coal can be oxidatively degraded into chemical fragments using trifluoroperoxyacetic acid which selectively oxidizes aromatic rings and is inert towards benzylic hydrogen. This procedure gives an excellent means for the determination of the aliphatic portions contained in the coal structure. These fragments contain more and different structural information relative to conventional oxidations with Mn(VII), Cr(VI), HNO_3 and O_2. These latter selectively oxidize benzylic hydrogen. Studies have also been performed using nitric acid as an oxidizing agent to analyze the amounts and lengths of linear alkane chains in the coal.

Once the methods of oxidative degradation were developed, the main problem was one of identifying the products obtained. It was observed that once the methyl esters of the products were made, the mixture could be separated using gas chromatography. Coupling the gas chromatograph with a mass spectrometer gave a technique that would separate and identify small amounts of complex products at the same time. It was for these reasons that this method was chosen.

A. Structure Identification

To identify the structures of the products obtained from the oxidative degradations of the coal, various analytical methods were used with the main procedure being gas chromatography/mass spectrometry

(GC/MS). Nuclear magnetic resonance (NMR) was used to examine the direct reaction mixture to determine the acetic acid content. Methanol can also be observed by this technique as can malonate and succinate if the line broadening is not too severe. Comparison of GC retention times to authentic samples provides another means of identifying compounds as well as spiking the samples with known compounds and then observing the change in the GC. Using this method and CIMS to determine the molecular weight, the long chain diacids were identified and are listed in Table 11. Perhaps the best method for the identification of unknown compounds is the preparation of a model compound and then comparison of the EIMS. This procedure will give a positive identification of the unknown and was used to identify most of the more abundant compounds. Identification was made, in the case of isomers, by comparison to known mixture GC retention times. Compounds identified by this procedure are listed in Table 12. Another method of positive identification is the direct comparison of EIMS of the unknown to those in the standard mass spectra library. Only one compound was identified by this procedure, 2-hydroxybutanedioic acid (MW = 162).

Although the above methods have identified many of the unknown compounds, the majority of the compounds were still unidentified. To attempt to identify these, some of the reaction mechanisms must be considered. In the PTFA reaction mixture, the active moiety is the OH^+ radical which attacks the electron rich sites in the coal structure first by hydroxylation, then ketonization, then insertion of an oxygen and then the elimination of CO_2. This process continues

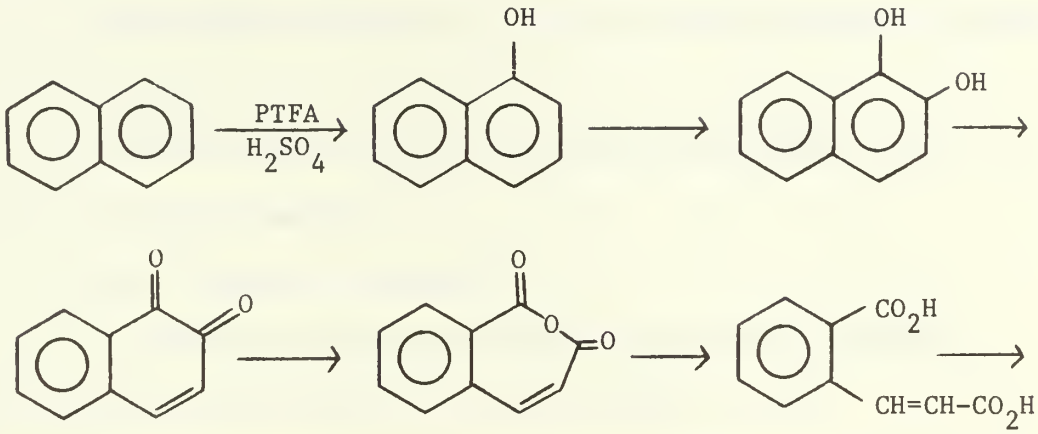
Table 11. Compounds Identified by Comparing GC Retention Times with Those of Authentic Samples

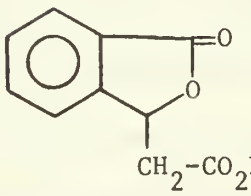
Molecular Weight	Name
118	Ethanedioic Acid
132	Propanedioic Acid
144	Cis-butenedioic Acid
146	Butanedioic Acid
160	2-Methylbutanedioic Acid
160	Pentanedioic Acid
174	x-Methylpentenedioic Acid
174	Hexanedioic Acid
188	x-Methylhexenedioic Acid
188	Heptanedioic Acid
202	Octanedioic Acid
216	Nonanedioic Acid
230	Decanedioic Acid
244	x-Methyldecanedioic Acid
244	Undecanedioic Acid
258	Dodecanedioic Acid
300	Pentadecanedioic Acid

Table 12. Compounds Identified by Comparison of GC Retention Times and Mass Spectra with Those of Authentic Samples

Molecular Weight	Name
162	Benzenepropenoic Acid
194A	Benzene-1,2-dicarboxylic Acid
194B	Benzene-1,4-dicarboxylic Acid
194C	Benzene-1,3-dicarboxylic Acid
204	2-Carboxybutanedioic Acid
208	Anthraquinone
218A	3-Carboxypentanedioic Acid
252A	Benzene-1,2,4-tricarboxylic Acid
252B	Benzene-1,2,3-tricarboxylic Acid
276A	2,3-Dicarboxypentanedioic Acid
310A	Benzene-1,2,4,5-tetracarboxylic Acid
310B	Benzene-1,2,3,5-tetracarboxylic Acid
368	Benzene-1,2,3,4,5-pentacarboxylic Acid

until a compound stable to the PTFA reagent is reached. The general sequence is demonstrated by:





MW = 206

with the products formed being greatly affected by the substitution on the rings. This example was chosen for two reasons. It demonstrates the proposed mechanism of the PTFA reaction; this compound is not seen in the products from coals, but it is seen from the oxidation of model compounds, and its diacid and triacid analogs are seen in the products from coals indicating that the rings are substituted or are of greater than two-ring systems.

The stability of various compounds to the PTFA reaction mixture have been studied with the following results:

1. Aldehydes are unstable.
2. Ketones are unstable.

3. Primary alcohols are stable, secondary alcohols are somewhat stable and tertiary alcohols are unstable.

4. Linear alkanes of up to C_7 are stable with the shorter chains being more stable.

5. Acids are stable and tend to stabilize aliphatic chains out to C_3-C_4 from their position.

6. Ether linkages are unstable.

7. The reaction mixture causes the lactonization of hydroxy acids when sterically possible (C_4 and C_5 hydroxy acids).

8. Aromatic rings which are substituted with electron withdrawing groups are stable.

9. Most sulfur compounds are soluble in the water wash work up procedure and are lost.

10. Aliphatic nitrogen compounds are unstable.

11. Tertiary carbons are unstable unless they are stabilized by a neighboring carboxyl.

This information rules out many of the possible structures for the remaining unknown compounds.

To tentatively identify the remaining compounds in Tables 2, 4 and 9, the following procedures were used. First, chemical ionization mass spectra were run and a molecular weight was determined for each compound. Then an electron impact mass spectra was run for each compound (EIMS for the unknown compounds are tabulated in Table 2 of the Appendix, for those compound identified by model studies, the EIMS of the models are tabulated in Table 3 of the Appendix). The chemical formula of four of the compounds was obtained by high

resolution mass spectrometry. Coupled with the fragmentation pattern from the EIMS, their structures were deduced. These four compounds are listed in Table 13.

It is convenient to identify each product by its MW. Thus 202 is the compound of MW 202. Where several products had the same MW, this is indicated by 202A, 202B, etc., the A, B, etc. indicating increasing GC retention times. It is also convenient to discuss the structures in terms of the parent acid using X to symbolize COOH.

The structure $XCH{=}CX_2$ is assigned to 202A on the basis that its EIMS and GC retention time was similar to 204 (XCH_2CHX_2). Similarly, 216A and 274 are dehydro derivatives of 218A and 276A. This gives a sequence of 202A plus one CH_2 group to go to 216A which goes to 274 when one more acid group is added.

A pyridine dicarboxylic acid structure was assigned to 195 because the EIMS is comparable to that of the benzene diacids. This makes 253 the pyridine tricarboxylic acid and 311 the pyridine tetracarboxylic acid analogous to the series of benzene polyacids. The odd MW indicated that 195, 253, and 311 contain one nitrogen atom. The pyridine structure was chosen because pyridine and quinoline were resistant to CF_3CO_3H oxidations whereas carbazole with a pyrrole ring and aliphatic amines were not.

The EIMS of 202B does not match that of 202A or of the C-8 linear chain diacid. The longer retention time (relative to other 202's) is evidence that it is a lactone. The base peak is P-87 which is attributed to the loss of $COOCH_3$ and CO, which is in accord with a

Table 13. Compounds Identified by High Resolution Mass Spectrometry

Molecular Weight	Name
218B	Oxiranetricarboxylic Acid
239	Pyridine-2,x,y-tricarboxylic Acid
276B	Oxiranetetracarboxylic Acid
297	Pyridine-2,x,y,z-tetracarboxylic Acid

carbomethoxy lactone. The homolog of 202B, 216B, was also observed and had a similar EIMS spectrum.

The EIMS of 220 is comparable to that of 234 so that 234 is a homolog of 220. The 220 species is proposed to be a carbomethoxy derivative of compound 162 (2-hydroxybutanedioic acid).

The EIMS of 208 is comparable to that of the benzene diacids and is assigned the 2-carboxybenzeneacetic acid structure. The 209 species is the nitrogen analog of 208 analogous to 195 being the nitrogen analog of the benzene diacids.

A possible mechanism for lactone formation was discussed earlier. There are three groups of these lactones. Although the compound shown in the reaction mechanism is not present, its diacid (264) and triacid (322) are seen with several isomers. The compound 206 is the homolog of 192; 250 and its isomers are carboxy derivatives of 192; and 308 and its isomers are dicarboxy derivatives of 192. The compound 210 is the cyclohexene analog of the 206 compound and the diacid 268 and the triacid 326 are carboxy and dicarboxy derivatives. The EIMS of these compounds shows their similarities.

The compound 290 has an EIMS similar to that of 276A and is considered to be a homolog.

This leaves only six compounds that have been included in Tables 2, 4 and 9 that cannot be related with the rest. These were tentatively identified by their molecular weight and interpretation of the EIMS as follows. The compound 158 shows only three peaks, a loss of 31, a loss of 59 and a peak at M/E = 59. This compound was identified as cis-2-methylbutenedioic acid because of its GC

retention time as compared to the cis-butenedioic acid and that it had been seen in model studies that would produce this compound. The compound 176 had two possible structures to fit the losses shown in the EIMS, but since one was an ether-type linkage, it was ruled out due to being unstable, leaving 2-methoxybutanedioic acid to fit the losses in the EIMS fo 59, 75 and 91. The compound 232 was determined to be a triacid compound by deuterated methanol studies. This was in accord with a P-177 peak in the EIMS spectrum. Also the assignment of the structure of an x-carboxyhexanedioic acid fits the losses of 59, 87 and 101 seen in the EIMS. There is more than one isomer of this compound detected in the coal samples. The compound 207 was seen in only the HNO_3 oxidation of the Wyodak coal sample. The EIMS shows a clear loss of 46 which is considered to be a loss of NO_2. The spectrum is similar to the EIMS of 162 (benzenepropenoic acid) compound except for the added NO_2. The last two compounds, 254 and 328, are the major components of the PTFA oxidation of PSOC-623. The 254 compound was a major product from fluoranthene. This greatly limits the possibilities and an acenaphthene tricarboxylic acid structure was assigned to the 328 compound as most likely. The 254 compound EIMS shows losses of 31, 59, 87 and 115 indicating it was a lactone, since these are typical losses from a monoacid lactone. It has a long GC retention time which supports this conclusion. Starting with the fluoranthrene model and attacking the electron rich double ring section, it can be seen how the devised structure was reached.

B. PTFA Oxidations of Parent Coals

The purpose of this part of the research project was two fold. The first and main emphasis was on structure identification of the products of the PTFA oxidative degradation of the parent coal samples. This was discussed in part A. The second objective was to determine if there was a simple correlation factor to be able to correlate the samples from one geographic area to another. For this purpose, 27 coal samples were chosen from the various provinces of the United States. The areas included in the various provinces are shown in Table 14. Another major concern in choosing the samples to be studied was the ranking of the coals. Coals are ranked, more or less, by increasing aromaticity. The relationship between volatility, aromaticity and rank is shown in Table 15.

An elemental analysis of the coal samples is shown in Table 1. From this Table, it can be seen that the elemental content of the various samples varies in the same manner within the same province as it does from one province to another and ranking varies, more or less, with carbon content, with the lignites having the lower carbon content. The carbon-to-hydrogen ratio by weight was calculated for the various samples. This again showed no consistancy when compared to ranking or geographic area.

The major components of PTFA oxidations are shown in Table 3. From the 27 samples, 104 different compounds were detected and from these 53 were chosen as the major components. The structures of these compounds were discussed in part A and are given in Table 2. The

Table 14. Coal Provinces of the United States

1. Eastern Province - Pennsylvania, West Virginia, Eastern Kentucky, Eastern Tennessee, Northern Alabama

2. Interior Province - Illinois, Indiana, Western Kentucky, Oklahoma, Kansas, Iowa, Missouri

3. Great Plains - North Dakota, Eastern Montana, Wyoming, North Eastern Colorado

4. Rocky Mountain - Southern Montana, South Western Wyoming, Utah, Central and Western Colorado, New Mexico, Arizona

5. Gulf - Southern Arkansas, Texas, Mississippi, Southern Alabama

6. Pacific - Washington, California, Oregon

7. Alaskan - Alaska

Table 15. Coal Ranking versus Volatility

% Volatility	Rank	Ranking	Aromaticity
↑	Lignites	↓	↓
	SBC		
	SBB		
	SBA		
	HVC		
	HVB		
	HVA		
	MED		
	LOW		
	Anthracities		

distribution of these compounds between the different coals can be seen in Table 3. Each sample contains on the average 25-30 compounds that comprises better than 80% of the GC area. The compounds are listed by molecular weight and relative GC retention time. The area given is the relative GC area and comparison from one coal sample to another was done by molecular weight and GC retention time as measured from the solvent peak.

The major points to be made from this study are:

1. The relative simplicity of the products obtained from the PTFA oxidation.

2. The sequencing of compounds from the diacids, to the triacids, to the tetraacids of the various compound types.

3. The near lack of the benzene dicarboxylic acids in the samples.

4. That ranking or carbon content did not correlate with the compounds produced or on their relative GC area.

5. The province from which the coal came from did not correlate with the compounds produced or on their relative GC areas.

6. The nitrogen content of the coal sample did not correlate with the amount of nitrogen-containing compounds produced.

7. There is no simple correlation factor that could be found to correlate the samples from one province to the next.

C. PTFA Oxidations of Solvent Refined Coals

The purpose of this section of the thesis was again two fold. The main emphasis was on the identification of the structures obtained

from the PTFA oxidations. These structures were discussed in part A. The second objective was to examine the changes in products due to solvent refining. Five bituminous coal samples were chosen for this study varying in ranking from HVC to low volatility. The five samples were furnished by Mobil Research and Development Corp. along with their soluble and insoluble fractions after three minutes solvent refining and the soluble fraction after 90 minutes.

Liquefaction (solvent refining) of coals involves thermolysis of benzyl oxygen and/or benzyl-benzyl bonds as the first step in the depolymerization of the coal. This view is derived from NMR studies,[29] studies with model compounds,[29,30] and oxidative degradations with $Na_2Cr_2O_7$[31] and $CF_3CO_3H_2$.[32]

Identification of the structures in Table 4 were discussed in part A. The major differences here is the relatively smaller number of products obtained from the oxidation process and the appearance of cis-2-methylbutenedioic acid (MW = 158), benzoic acid (MW = 136), 2-carboxybenzeneacetic acid (MW = 208), 3-carboxypyridine-2-acetic acid (MW = 209), phthalide-3-carboxylic acid (MW = 192), and x-carboxyphthalide-3-carboxylic acid (MW = 250), all of which are characteristic of aromatic systems. The distribution of the products is shown in Table 5.

Perhaps the best method for determining the amount of arylmethyl in coals is from the yield of acetic acid formed in the oxidative degradation with trifluoroperoxyacetic acid.[12,32,33] The acetic acid content is measured by NMR of the direct reaction mixture. The data from this method is shown in Table 16.

Table 16. Yields of Acetic Acid from Oxidative Degradations of CF_3CO_3H-H_2SO_4

Name	Penn State Coal Base Number[a] 372 Kentucky Imboden	330 Penn. Middle Kittaning	256 Penn. Lower Freeport	312 Arizona Red	405 Oklahoma Lower Hartshorne
% Liquified (3 min)[a]	79	70	65	51	25
% C (maf)	85.9	83.5	88.2	78.4	89.8
Rank	HVA	HVB	med. vol.	HVC	low vol.
	Yield of Acetic Acid (meq. per g of maf)[b]				
Parent coal	0.44	0.33	0.31	0.42	0.31
SRC (3 min)	0.77	0.74	1.05	1.46	1.51
SRC (90 min)	1.45	1.15	1.06	1.60	1.69
Residue (3 min)	0.33	0.41	0.27	0.27	0.24

[a]Samples and liquefaction data were supplied by D. D. Whitehurst, Mobil Research and Development Corp.

[b]The percentages of moisture (m) and ash (a) are available from the Penn State Coal Base computer printouts. The SRC samples had negligible moisture or ash. In calculating the yields of acetic acid from the residue, it was assumed that all of the ash in the coal was retained in the residue in correcting to a maf (moisture and ash free) basis.

From the data in Tables 4, 5 and 16, the following chemical changes due to coal liquefaction were noted:

1. A sharp increase in arymethyl accompanies liquefaction in all the samples.

2. All five coal samples give about the same percentage increase in arylmethyl after 90 minutes of solvent refining but not after three minutes. This indicates that benzyl radicals form from more than one type structure.

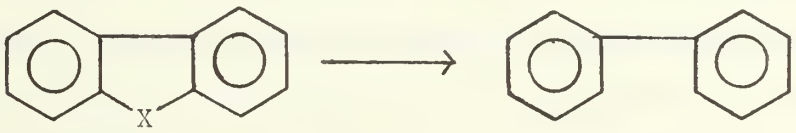
3. The amount of arylmethyl in the residue is about the same as in the original coal. This indicates that arylmethyls do not play any role in liquefaction as expected. Arylmethyl is approximately 1% of the carbon content in the parent coals and residues and increases to 2-3% upon liquefaction.

4. No higher homologs of acetic acid were observed indicating the absence of arylalkyls above methyl.

5. It might have been expected that the more the arylmethyl, the more cleavage, and the more SRC. In fact the opposite is true. The conflict would be resolved if coal liquefaction depended more on certain critical cleavages and the conversion of a 3-dimensional polymer to a 1-dimensional polymer than on the total amount of cleavage and the extent of depolymerization.

6. Biaryl structures are rare or absent in the original coals but appear in significant quantity on liquefaction. This is evidenced by the increase in benzoic acid upon liquefaction. Benzoic acid is a major product of the PTFA oxidation of the biaryl structure.

7. The increase in the benzene-1,4 and 1,3-dicarboxylic acids and benzene-1,3,5-tricarboxylic acid are more characteristic of biaryl structures in contrast to fused aromatics which form products with adjacent (1,2) carboxyls. This increase in biaryl structure is viewed to come from the following type structures



X = heteroatom (S, O, etc.)

with the heteroatom being easily removed by liquefaction.

8. Aromatic structure increases on liquefaction. This is evidenced by the increase in benzene-1,2-dicarboxylic acid, which is the dominant product from most polyaromatic systems. Also by the appearance of certain lactones which are minor products from oxidation of a variety of polyaromatic hydrocarbons, in the oxidation products of the SRC but not in the original coal.

9. Oxidation of coals with 40% HNO_3 provides a reliable method for determining the amounts and lengths of linear alkane chains in coal (HNO_3 oxidations will be discussed later). As expected the amounts and lengths of the linear chains showed no change on solvent refining.

D. PTFA Oxidation of Model Compounds

Model compounds have been extensively studied using the PTFA oxidation in an attempt to determine the type of structure that the

products seen from PTFA oxidation of coals, are coming from in an attempt to correlate these back to the original structures of coals.[34] For the purpose of this discussion, nine models were chosen for oxidation with PTFA, as disucssed earlier, ranging from purely aromatic to dihydroaromatic to purely alaphatic. The products obtained from the model compounds are compared to the major component products from the PTFA oxidation of the parent coals and solvent refined coals. The results of this comparison are shown in Table 8.

From this study, the following important points were noted:

1. Decalin, a purely alaphatic compound, gave only the straight chain diacids of malonic, succinic, glutaric and adipic acids and one of the butane triacids, accounting for 84.1% of the total GC area. There was no change in the area accounted for between the parent and SRC coal samples indicating that there is no effect on the cyclo alaphatic portion of the coals on solvent refining.

2. The purely aromatic models, pyrene, perylene and fluoranthrene, show virtually no short chain diacids but do show large percentages of the benzene diacids and the lactones seen in the solvent refined coal samples. The benzene-1,2,4-tricarboxylic acid is present but there is an absence of the benzene tetraacids. There was a general trend to increase in area accounted for in going from the parent coals to the SRC's, indicating, again, that the aromaticity of the coal is increased on solvent refining.

3. The dihydroaromatic models show the lower short chain diacids and the benzene polyacids giving a distribution that closer resembles that of the coal samples. These models also show an increase in GC

area accounted for in the solvent refined coal comparison. This comparison to the coal samples gives evidence of the hydroaromatic structures being present in the original coal structures.

4. The models show a large percentage of the benzene diacids. This is not the case in the majority of the coal samples. The benzene-1,4- and 1,3-dicarboxylic acids decrease in abundance on going to the dihydroaromatic structure and all of the benzene diacids show a marked decrease when the dihydro positions are substituted, as in the maleicanhydride-anthracene adduct. This model also shows the butane triacid (MW = 232) that is generally seen in the place of the benzene diacids in the coal samples, the x,y-dicarboxybutanolide (MW = 202B), the x,y-dicarboxypentanolide (MW = 216B) and both isomers of the x,y-dicarboxyhexanedioic aicd (MW = 290), all of which are seen in the parent and solvent refined coals. This is the only model studied that shows these compounds and this indicates that the dihydro positions in the coals serve as connecting points in the original coal structure, possibly to form a 3-dimensional structure.

E. Nitric Acid Oxidations of Parent Coals

Many lines of evidence suggest that coals are composed of aromatic rings, singly or in small clusters, connected to each other by aliphatic structures. The key question is what is the nature of these aliphatic connectors. Are they non-cyclic (methylene, ethylene, or longer chain) and/or are they cyclic hydroaromatic units fused to the aromatic rings? Hydroaromatic structures have been implicated because of the increase in aromaticity which is evident on thermal

treatment and the increase in aromatic structure with increase in rank and colification as discussed in part C.

It has been found that 40% aqueous nitric acid at 60°C oxidatively cleaves alcohols, ketones and alkylbenzenes to form carboxylic acids. The aliphatic and aromatic carboxylic acids do not react further in general, and specifically, alkane chains do not react appreciably below 80°C. The reaction is an excellent method for determining the amounts and lengths of saturated linear alkane chains in coals.[35] Table 10 summarizes the data on six coal samples chosen for oxidation by 40% nitric acid. The structures of these compounds are shown in Table 9 and were discussed earlier.

To illustrate the interpretations of Table 10, a 1,8-diphenyloctane would produce adipic acid so that the yield of the six-carbon adipic acid measures the amount of eight-carbon alkane chains in the coals. The fraction of carbon in such chains varied from 0.4-2.3% in five of the six coals. In the sixth, it accounted for 42% of the carbon, and diacids out to C_{40} were observed.

The important points noted from this study were as follows:

1. HNO_3 (40%) at 60°C produced linear diacids from alcohols, ketones and alkylbenzenes but would not degrade them further.

2. No interference should arise from simple arylalkyl groups. Alkyls would be signaled by the appearance of monoacids and none were detected.

3. No interference should arise from occluded hydrocarbons in coal. The amounts of these seem to be small based on extraction

experiments. Even if small amounts reacted, monoacids would be the initial products and none were detected.

4. The yields of linear diacids vary in a smooth continuous manner. It is possible that the chains are of a single length or a few selected lengths, and that an oxidizable group such as CH=CH or even a methyl branch is distributed non-selectively in each chain.

5. There is an absence of monoacids and nitro compounds indicating that the linear alkane chains are attached at both ends to some oxidizable and cleavable group. The most likely attachment would be to an aromatic system.

6. Propylbenzene, isopropylbenzene and 9,10-dihydroanthracene were oxidized. Benzoic acid was by far the dominant product from the two propylbenzenes and anthraquinone predominated from the dihydro-anthracene. This showed that benzylic positions are oxidatively cleaved regardless of whether they are secondary, tertiary or cyclic.

F. Quantitative Studies

All quantitative measurements reported in this work were done using an internal standard, both in NMR and GC results, and then comparing the peak areas to that of the known standard. For the GC areas, the peak areas were first corrected for effective carbon number to account for differences in detector response to different functional groups. The correction factors are listed in Table 6.

Absolute yields of the major components of the solvent refined coals were calculated and are listed in Table 7. This results shows that the absolute yield from the PTFA oxidations is on the order of

8-9%. Similar calculations have been made for the nitric acid oxidations and the yields are on the same order. These studies indicated that there is not very much material recovered and/or the methods used to detect the products are not that quantitative.

To better understand these results, the following points were noted:

1. Since the oxidative procedures used were developed to observe the aliphatic portions of coals, large yields were not expected since previous studies indicated coals contained large percentages of aromatic structures.

2. The work-up procedure includes several washes with water and such products as sulfur-containing compounds and other water soluble products would be lost along with any mineral matter contained.

3. The PTFA reaction mechanism allows for the burning away of the unsubstituted aromatic rings in the form of CO_2. The CO_2 can be observed escaping during the reaction time. This gives a considerable loss of carbon content.

4. The comparison of absolute yields of one component to another are somewhat speculative due to the different stabilities of the various types of functional groups to the reaction mixture and because some of the compounds, especially the higher benzene polyacids, will decarboxylate to a lower homolog.

5. Differences in absolute yields of the same sample have been noted between NMR and GC measurements indicating that all of the sample may not be volatile and is simply remaining on the top of the GC column used.

For the above reasons, this oxidative procedure is not considered to be very applicable to the quantitative measurement of the products obtained.

APPENDIX

Table 1. PTFA Oxidations of Parent Coals

Province	Sample	State	Name	188 (2.99)	132 (4.36)	144 (5.64)	130 (5.61)	146 (6.04)
Eastern	DJR-71 (PSOC-256)	PA	PA Lower Freeport	---	10.9	1.3	0.1	3.4
	DJR-67 (PSOC-330)	PA	PA Middle Kittaning	---	29.1	0.2	---	6.1
	PSOC-349	PA	PA Lower Clarion	---	---	---	---	0.4
	PSOC-124	WV	WV Lower Kittaning	---	19.7	1.5	4.8	17.2
	PSOC-372	KY	KY Imboden	---	---	---	---	---
	PSOC-308	OH	OH #5	---	---	---	---	0.2
Interior	PSOC-641	KY	KY #6	---	---	---	---	---
	DJR-47	IL	IL #6 Monterey	1.4	16.2	0.6	---	2.5
	DJR-44	IL	IL #6 Burning State	---	3.7	0.7	---	2.5
	PSOC-582	IL	IL #5	---	---	---	---	---
	PSOC-399	OK	OK Fort Scott	---	---	---	---	0.1
	DJR-69 (PSOC-405)	OK	OK Lower Hartshorng	---	6.2	0.5	---	8.3
Rocky	PSOC-155	UT	UT Mesa Verde	---	---	---	---	---
Mountain	PSOC-453	UT	UT Blind Canyon	---	11.9	1.3	---	10.0
	PSOC-459	UT	UT Lower Sunnyside	---	7.9	0.8	---	9.2
	PSOC-500	UT	UT Hiawatha	---	11.2	---	---	8.9
	PSOC-503	UT	UT Upper Sunnyside	---	---	---	---	---
	DJR-66 (PSOC-312)	AZ	AZ Red	---	16.4	1.4	---	10.1
	PSOC-450	CO	CO Upper B	---	0.4	---	---	0.3
Great	DJR-70	ND	ND Lignite	---	4.2	1.6	---	8.7
Plains	DJR-29	WY	Wyodak	---	---	---	---	---
	PSOC-535	MT	MT Dietz	---	10.6	2.0	---	12.0
Gulf	PSOC-418	TX	TX Lignite	---	---	---	---	---
	PSOC-623	TX	Darco TX Lignite	---	2.0	---	---	1.8
Pacific	PSOC-95	WA	WA Queen #4	---	16.4	---	0.5	8.5
Alaskan	DJR-37 (POC-339)	AK	Alaskan	---	4.1	---	---	3.4
	DJR-39 (POC-340)	AK	Alaskan	---	0.5	---	---	1.4

Table 1. (continued)

Sample	148 (6.48)	160 (6.52)	136 (6.72)	176 (7.24)	180 (7.41)	160 (7.52)	162 (7.98)	158 (8.75)	174 (9.20)	188 (10.12)
DJR-71 (PSOC-256)	---	---	---	0.5	0.9	---	0.6	---	---	0.4
DJR-67 (PSOC-330)	---	1.1	---	0.8	---	1.3	1.0	---	0.1	0.4
PSOC-349	---	---	---	---	---	1.0	1.0	---	---	1.2
PSOC-124	---	---	---	---	---	5.7	---	---	0.6	---
PSOC-372	---	---	---	---	---	---	---	2.3	---	---
PSOC-308	---	---	---	1.0	---	---	0.9	---	---	0.6
PSOC-641	---	---	---	---	---	---	---	2.7	2.0	---
DJR-47	---	---	---	2.3	---	1.4	1.6	---	0.3	1.6
DJR-44	---	3.2	---	---	---	2.9	3.7	---	---	3.1
PSOC-582	---	---	---	---	---	---	---	---	---	2.8
PSOC-399	---	0.7	---	---	---	0.6	1.6	---	---	1.0
DJR-69 (PSOC-405)	---	1.7	---	2.1	---	---	2.4	---	0.7	---
PSOC-155	---	---	---	---	---	---	---	---	---	---
PSOC-453	---	2.5	0.9	---	---	1.9	---	0.1	0.3	---
PSOC-459	---	1.7	0.5	---	---	1.2	---	0.2	---	---
PSOC-500	---	2.7	---	---	---	2.1	1.9	---	---	---
PSOC-503	---	0.6	---	---	---	0.5	0.3	---	---	---
DJR-66 (PSOC-312)	7.2	1.3	---	1.6	---	---	6.1	0.4	---	---
PSOC-450	---	---	---	---	---	0.2	---	---	---	---
DJR-70	---	2.2	---	---	---	6.0	0.5	---	---	0.4
DJR-29	---	---	---	0.6	---	2.9	3.1	---	---	---
PSOC-535	---	3.1	---	---	---	3.3	0.4	0.4	0.4	---
PSOC-418	---	---	---	---	---	---	---	1.5	---	---
PSOC-623	---	---	---	---	---	0.3	---	---	---	0.5
PSOC-95	---	1.4	---	---	---	3.7	0.3	---	0.2	---
DJR-37 (POC-339)	---	2.1	---	---	---	2.0	0.8	---	0.3	---
DJR-39 (PCO-340)	6.1	4.5	---	---	---	5.7	---	---	1.4	---

Table 1. (continued)

Sample	144 (10.27)	204 (10.49)	218 (10.73)	202 (11.27)	220 (11.46)	218A (11.82)	218B (12.32)	194A (12.62)	232 (12.63)
DJR-71 (PSOC-256)	---	13.4	---	0.7	2.5	4.7	11.3	---	5.9
DJR-67 (PSOC-330)	---	12.7	---	0.6	2.8	4.6	13.2	---	---
PSOC-349	---	14.3	---	---	3.6	7.8	5.8	5.5	---
PSOC-124	---	4.3	---	---	2.0	11.3	5.9	---	2.3
PSOC-372	---	1.6	---	1.9	---	10.9	2.7	1.0	---
PSOC-308	---	8.8	---	1.8	3.8	10.9	4.0	1.7	---
PSOC-641	---	9.7	---	---	3.0	5.1	15.4	---	4.7
DJR-47	---	10.8	---	0.9	2.2	5.3	17.7	---	3.1
DJR-44	---	11.5	---	1.4	3.1	8.7	11.2	---	5.4
PSOC-582	---	14.5	---	0.2	2.1	5.0	19.9	---	1.6
PSOC-399	---	9.0	---	1.5	2.5	5.1	4.7	---	3.4
DJR-69 (PSOC-405)	0.7	2.7	---	2.2	---	9.1	6.4	6.5	---
PSOC-155	0.8	---	---	---	---	3.6	2.2	---	2.0
PSOC-453	---	4.0	---	0.8	---	3.4	3.8	0.7	---
PSOC-459	0.5	2.1	---	1.6	---	4.6	2.8	2.1	---
PSOC-500	---	4.6	---	1.2	2.4	5.7	10.4	---	4.2
PSOC-503	0.9	7.9	---	---	1.6	6.8	14.6	---	7.6
DJR-66 (PSOC-312)	1.4	4.7	---	1.5	---	6.6	2.8	---	---
PSOC-450	---	2.1	---	1.5	---	5.7	3.9	1.9	---
DJR-70	---	12.6	---	0.6	0.6	7.5	9.3	---	8.6
DJR-29	3.0	---	---	3.5	---	10.0	3.8	---	3.4
PSOC-535	0.4	4.8	---	2.4	---	6.2	7.0	---	4.4
PSOC-418	---	12.9	---	3.6	---	15.4	13.0	---	---
PSOC-623	---	2.2	---	---	0.3	1.5	3.5	---	2.1
PSOC-95	0.3	9.3	---	1.7	---	5.2	7.1	---	3.1
DJR-37 (POC-339)	2.6	3.3	---	3.1	---	10.8	13.1	---	---
DJR-39 (POC-340)	---	10.7	2.4	0.4	1.2	6.3	8.7	---	8.4

Table 1. (continued)

Sample	234 (12.78)	194B (12.93)	195 (13.01)	216 (13.23)	232 (13.32)	282 (13.39)	202 (13.43)	228 (13.48)	194 (13.62)
DJR-71 (PSOC-256)	---	---	0.9	0.8	---	---	1.6	---	---
DJR-67 (PSOC-330)	3.6	---	---	0.5	---	---	0.6	---	---
PSOC-349	---	---	---	2.2	---	---	---	---	---
PSOC-124	0.8	---	---	---	1.0	---	---	---	---
PSOC-372	1.2	---	0.8	1.6	---	1.7	---	---	---
PSOC-308	3.2	---	3.3	2.3	2.4	---	---	---	---
PSOC-641	---	---	---	---	7.6	---	---	5.1	---
DJR-47	---	---	0.4	---	---	---	---	---	---
DJR-44	---	4.5	---	---	---	---	---	---	---
PSOC-582	3.9	---	---	---	---	---	---	---	---
PSOC-399	---	---	---	1.1	---	---	---	---	---
DJR-69 (PSOC-405)	1.3	2.6	---	---	---	---	1.9	---	---
PSOC-155	---	---	---	---	0.2	---	---	---	---
PSOC-453	---	3.5	---	---	0.9	---	1.5	---	7.4
PSOC-459	---	2.2	---	1.2	---	---	---	---	1.0
PSOC-500	---	---	---	0.5	0.4	---	1.2	---	---
PSOC-503	---	---	---	1.9	---	---	2.1	---	---
DJR-66 (PSOC-312)	2.5	---	---	3.5	---	---	---	---	---
PSOC-450	---	---	2.9	1.1	1.3	---	---	---	---
DJR-70	5.1	---	---	2.5	---	---	---	---	---
DJR-29	3.3	---	---	2.0	4.2	---	2.5	---	---
PSOC-535	---	0.9	---	---	1.7	---	1.8	---	---
PSOC-418	2.9	---	---	3.1	---	---	---	---	---
PSOC-623	---	---	---	---	0.1	---	0.3	---	---
PSOC-95	---	---	0.7	0.8	---	---	0.9	---	---
DJR-37 (POC-339)	3.6	---	---	1.3	---	---	0.9	---	---
DJR-39 (POC-340)	---	---	---	2.2	---	---	---	---	---

Table 1. (continued)

Sample	250 (13.69)	202 (13.79)	195 (13.84)	210 (13.92)	262 (14.04)	232 (14.26)	186 (14.49)	260 (14.54)	216 (14.58)
DJR-71 (PSOC-256)	---	---	---	2.5	---	---	---	---	1.3
DJR-67 (PSOC-330)	---	---	0.3	---	0.4	1.7	---	---	1.7
PSOC-349	---	0.4	---	---	---	1.0	---	---	1.2
PSOC-124	---	---	---	---	---	---	---	---	---
PSOC-372	---	0.8	---	1.8	---	---	---	---	0.5
PSOC-308	---	---	2.5	---	---	---	---	---	1.7
PSOC-641	---	---	---	2.6	2.2	---	---	---	3.0
DJR-47	---	0.1	---	2.4	---	0.4	---	---	1.9
DJR-44	---	---	---	2.6	---	---	---	---	---
PSOC-582	3.3	1.2	---	3.4	---	0.9	---	---	---
PSOC-399	---	---	1.7	2.1	1.5	2.1	---	---	1.7
DJR-69 (PSOC-405)	---	---	---	4.9	---	---	---	---	2.1
PSOC-155	---	---	0.3	---	0.4	1.7	---	---	1.7
PSOC-453	---	---	---	---	---	---	---	---	1.6
PSOC-459	---	0.9	---	---	---	0.3	13.2	---	---
PSOC-500	0.5	0.5	---	---	---	0.4	---	---	1.3
PSOC-503	1.2	1.4	---	---	---	1.7	---	---	1.3
DJR-66 (PSOC-312)	---	0.6	---	0.7	---	---	---	---	0.6
PSOC-450	---	---	1.4	---	---	1.4	---	---	1.6
DJR-70	---	0.3	---	---	0.9	---	---	2.3	0.3
DJR-29	---	1.2	---	---	---	4.1	---	---	4.4
PSOC-535	---	---	---	1.9	---	---	---	---	1.5
PSOC-418	---	0.9	1.9	---	---	---	---	---	2.1
PSOC-623	---	---	---	0.1	---	---	---	---	---
PSOC-95	---	---	---	1.8	---	---	---	---	2.4
DJR-37 (POC-339)	---	1.1	---	---	---	---	---	---	2.0
DJR-39 (POC-340)	3.2	---	---	---	1.9	0.9	---	---	2.5

Table 1. (continued)

Sample	230 (14.74)	216 (14.80)	236 (14.89)	289 (15.05)	210 (15.09)	216 (15.17)	288 (15.20)	276 (15.20)	274 (15.21)
DJR-71 (PSOC-256)	---	---	---	---	---	---	---	1.8	---
DJR-67 (PSOC-330)	---	0.1	---	---	---	---	---	1.3	---
PSOC-349	---	1.0	---	---	---	2.5	---	1.3	---
PSOC-124	---	1.0	---	---	---	---	---	0.4	---
PSOC-372	---	2.4	---	1.2	---	0.6	---	---	---
PSOC-308	---	3.7	---	---	---	3.8	---	---	---
PSOC-641	0.1	---	---	---	---	---	---	2.3	---
DJR-47	---	0.1	---	---	---	---	---	1.7	---
DJR-44	---	---	---	3.3	---	---	---	3.8	---
PSOC-582	---	---	---	---	---	---	---	0.6	---
PSOC-399	3.2	---	---	---	---	---	---	1.1	---
DJR-69 (PSOC-405)	---	0.2	---	---	2.2	---	---	---	---
PSOC-155	---	0.1	---	---	---	---	---	---	---
PSOC-453	0.5	---	---	---	---	---	---	---	---
PSOC-459	---	---	---	---	---	---	---	---	---
PSOC-500	0.2	---	---	---	---	---	---	0.2	---
PSOC-503	---	2.1	---	---	---	0.1	0.4	---	---
DJR-66 (PSOC-312)	---	2.5	0.2	---	---	---	---	0.5	---
PSOC-450	---	---	---	---	---	---	---	---	---
DJR-70	---	1.2	---	---	---	---	---	0.8	---
DJR-29	---	1.8	---	---	---	---	---	---	---
PSOC-535	---	0.2	---	---	---	0.3	---	---	---
PSOC-418	0.6	4.0	---	---	---	---	---	1.8	---
PSOC-623	---	0.2	---	---	---	---	---	0.2	---
PSOC-95	---	---	---	---	---	1.1	---	---	---
DJR-37 (POC-339)	3.7	---	---	---	---	1.0	---	---	---
DJR-39 (POC-340)	---	1.7	---	---	---	---	---	0.1	2.2

Table 1. (continued)

Sample	216 (15.35)	226 (15.52)	276 (15.77)	239 (16.07)	290 (16.40)	290 (16.68)	288 (16.71)	274 (16.97)	274 (17.20)
DJR-71 (PSOC-256)	---	---	7.4	---	---	---	---	---	---
DJR-67 (PSOC-330)	---	---	5.4	---	0.5	0.5	---	0.1	1.6
PSOC-349	---	1.1	5.8	---	1.3	1.7	---	1.2	---
PSOC-124	---	---	2.9	---	0.6	1.0	---	0.2	---
PSOC-372	1.0	---	4.7	0.9	1.5	---	---	0.7	---
PSOC-308	---	---	6.8	---	1.9	1.3	---	0.8	3.4
PSOC-641	1.2	---	5.0	---	2.2	4.1	---	1.9	---
DJR-47	---	0.8	7.2	---	1.3	2.2	---	---	---
DJR-44	---	---	4.7	---	1.4	2.1	---	---	---
PSOC-582	---	---	17.0	---	0.6	2.9	---	1.2	2.1
PSOC-399	---	---	9.3	---	1.0	2.8	---	0.8	3.5
DJR-69 (PSOC-405)	1.1	---	4.7	---	0.8	0.5	---	---	---
PSOC-155	---	---	---	---	---	1.0	---	---	---
PSOC-453	---	---	2.9	---	0.1	0.2	---	---	---
PSOC-459	0.5	---	1.5	0.3	0.6	---	---	---	---
PSOC-500	---	---	6.4	---	1.6	1.6	---	---	---
PSOC-503	0.5	---	9.9	---	1.0	1.4	---	---	---
DJR-66 (PSOC-312)	---	---	5.8	---	1.0	---	---	0.4	---
PSOC-450	---	---	4.2	2.1	0.6	---	---	---	---
DJR-70	---	---	11.6	---	1.5	0.4	---	1.5	1.7
DJR-29	---	---	11.9	---	1.9	---	0.7	5.8	---
PSOC-535	0.4	---	3.0	---	1.1	1.1	---	0.3	---
PSOC-418	---	---	14.1	---	---	2.2	1.5	1.1	3.3
PSOC-623	---	---	1.2	---	0.1	---	---	---	---
PSOC-95	---	---	5.9	---	0.9	0.4	---	0.2	2.2
DJR-37 (POC-339)	---	---	25.7	---	2.5	---	0.7	---	---
DJR-39 (POC-340)	---	---	3.7	---	1.3	2.4	---	0.8	---

Table 1. (continued)

Sample	252 (17.24)	253 (17.59)	252 (17.63)	290 (18.09)	290 (18.29)	268 (18.31)	288 (18.45)	253 (18.63)	282 (18.81)
DJR-71 (PSOC-256)	5.3	0.7	---	---	---	2.4	---	2.8	---
DJR-67 (PSOC-330)	---	1.0	---	---	---	---	3.4	0.6	---
PSOC-349	5.1	1.3	---	---	---	2.1	---	---	---
PSOC-124	4.8	0.5	---	---	---	5.1	---	---	---
PSOC-372	3.5	0.8	---	---	---	---	---	---	---
PSOC-308	---	4.0	---	1.7	---	---	---	6.2	---
PSOC-641	---	3.1	---	---	---	11.0	2.1	---	1.7
DJR-47	4.5	---	1.5	---	---	2.3	---	---	---
DJR-44	3.2	0.6	---	---	---	2.8	---	---	---
PSOC-582	---	1.7	---	0.4	---	---	---	0.8	---
PSOC-399	---	4.2	---	1.2	1.3	---	---	3.8	---
DJR-69 (PSOC-405)	5.0	0.5	---	---	---	2.4	---	---	---
PSOC-155	1.9	---	---	---	---	---	---	---	---
PSOC-453	1.0	---	0.4	---	---	---	---	---	---
PSOC-459	6.4	---	---	---	---	1.5	---	---	---
PSOC-500	5.7	0.3	---	---	---	0.8	---	---	---
PSOC-503	5.0	1.2	---	0.8	---	4.0	---	---	---
DJR-66 (PSOC-312)	4.0	0.6	---	---	---	1.6	---	0.6	---
PSOC-450	2.5	3.2	---	---	---	4.2	---	---	---
DJR-70	---	1.3	---	---	---	---	1.1	---	---
DJR-29	8.2	1.5	---	---	---	1.9	0.2	---	---
PSOC-535	5.4	---	0.5	---	---	1.6	---	---	---
PSOC-418	---	1.5	---	---	---	3.1	---	---	---
PSOC-623	0.8	---	---	---	---	0.2	---	---	---
PSOC-95	---	2.1	---	---	---	5.3	---	0.6	---
DJR-37 (POC-339)	9.6	0.8	---	---	---	0.9	---	---	---
DJR-39 (POC-340)	3.6	1.5	---	1.8	---	1.8	---	---	---

Table 1. (continued)

Sample	268 (18.86)	264 (19.02)	208 (19.03)	296 (19.13)	268 (19.14)	268 (19.51)	297 (19.61)	260 (19.70)	250 (19.73)
DJR-71 (PSOC-256)	---	---	---	1.0	---	---	1.6	---	---
DJR-67 (PSOC-330)	---	---	---	---	---	---	---	---	---
PSOC-349	---	---	---	---	---	---	---	---	---
PSOC-124	---	22.4	---	---	---	---	1.7	---	---
PSOC-372	---	---	42.7	---	1.3	---	0.8	---	2.6
PSOC-308	---	2.7	---	---	---	---	1.3	---	---
PSOC-641	4.1	---	---	---	2.8	2.4	1.3	---	---
DJR-47	3.4	---	---	---	---	---	---	1.6	---
DJR-44	4.7	---	---	---	---	0.9	---	---	---
PSOC-582	---	---	---	---	---	---	---	---	---
PSOC-399	---	1.1	---	---	---	---	0.9	---	---
DJR-69 (PSOC-405)	---	---	---	---	---	---	---	---	2.3
PSOC-155	---	---	82.4	---	---	---	---	---	---
PSOC-453	1.2	---	---	---	13.5	---	1.3	---	---
PSOC-459	---	---	---	---	25.8	---	1.8	---	---
PSOC-500	3.6	1.4	---	---	3.1	---	3.4	---	---
PSOC-503	---	4.5	---	---	---	---	2.8	---	---
DJR-66 (PSOC-312)	2.5	---	1.6	---	---	---	---	---	1.4
PSOC-450	6.0	6.2	---	---	---	---	7.1	---	---
DJR-70	---	---	---	---	---	---	---	---	---
DJR-29	2.9	---	---	---	1.8	---	---	---	0.6
PSOC-535	---	---	---	---	5.2	0.7	---	---	0.5
PSOC-418	---	---	---	---	---	---	---	---	---
PSOC-623	---	0.3	3.6	---	---	---	---	---	---
PSOC-95	---	---	---	1.4	---	---	2.6	---	---
DJR-37 (POC-339)	---	---	---	---	---	---	---	---	---
DJR-39 (POC-340)	---	---	---	---	---	---	---	1.5	---

Table 1. (continued)

Sample	294 (19.89)	250 (20.13)	297 (20.13)	268 (20.17)	310 (20.52)	295 (20.85)	311 (21.00)	310 (21.05)	338 (21.51)
DJR-71 (PSOC-256)	0.7	---	---	---	7.4	---	2.8	---	0.1
DJR-67 (PSOC-330)	---	---	---	---	2.1	---	1.5	---	---
PSOC-349	---	---	---	3.4	0.8	---	0.7	---	---
PSOC-124	---	---	---	---	3.9	---	---	2.0	---
PSOC-372	---	---	---	---	3.4	---	0.8	---	0.1
PSOC-308	---	---	---	---	4.6	---	3.6	---	---
PSOC-641	---	---	---	0.9	3.9	---	---	1.2	---
DJR-47	---	---	---	---	2.2	---	---	1.1	---
DJR-44	---	---	---	---	1.5	---	1.6	---	---
PSOC-582	---	---	---	---	1.2	---	8.1	---	---
PSOC-399	---	---	---	---	3.1	---	7.0	---	---
DJR-69 (PSOC-405)	2.2	2.3	---	---	1.9	0.7	1.2	---	0.7
PSOC-155	---	---	---	---	2.2	---	---	---	---
PSOC-453	3.5	---	---	---	5.3	---	---	1.4	---
PSOC-459	3.3	---	---	---	3.0	---	---	1.5	---
PSOC-500	1.9	---	---	---	5.4	---	---	1.9	---
PSOC-503	---	---	---	---	6.7	---	---	1.4	---
DJR-66 (PSOC-312)	---	---	---	---	4.0	---	---	1.3	---
PSOC-450	---	---	3.5	---	7.8	---	---	3.3	---
DJR-70	---	---	---	---	1.2	---	0.7	---	---
DJR-29	---	---	---	---	4.0	---	0.2	0.6	---
PSOC-535	0.5	---	---	---	2.7	---	---	0.9	---
PSOC-418	---	---	---	---	5.2	---	---	2.0	---
PSOC-623	---	---	---	---	0.5	---	---	---	---
PSOC-95	---	---	---	---	6.9	---	0.5	---	---
DJR-37 (POC-339)	---	---	---	---	0.4	---	0.1	---	---
DJR-39 (POC-340)	---	---	---	---	4.2	---	---	0.9	---

Table 1. (continued)

Sample	338 (21.85)	322 (21.18)	352 (22.18)	308 (22.19)	322 (22.57)	322 (22.65)	312 (22.68)	326 (22.97)	338 (23.02)
DJR-71 (PSOC-256)	0.4	---	---	0.7	---	---	---	---	---
DJR-67 (PSOC-330)	---	---	---	0.5	---	---	---	---	---
PSOC-349	---	---	---	1.3	---	---	---	---	---
PSOC-124	---	---	---	0.6	---	---	---	---	---
PSOC-372	---	---	0.7	---	---	---	---	---	---
PSOC-308	---	2.7	0.8	---	---	---	---	1.8	---
PSOC-641	---	---	---	0.3	---	---	---	---	---
DJR-47	---	---	---	0.1	---	---	---	---	---
DJR-44	---	---	---	0.5	---	---	---	---	---
PSOC-582	---	---	---	---	---	---	4.3	---	---
PSOC-399	---	2.2	---	2.1	2.2	---	---	---	2.6
DJR-69 (PSOC-405)	1.1	---	2.2	---	---	0.6	---	---	0.7
PSOC-155	---	---	---	---	---	---	---	---	---
PSOC-453	---	---	---	0.2	---	---	---	---	---
PSOC-459	---	---	---	0.5	---	---	---	---	---
PSOC-500	---	---	---	1.4	---	---	---	1.6	---
PSOC-503	---	0.5	---	0.4	1.9	1.0	---	---	---
DJR-66 (PSOC-312)	---	---	---	0.3	---	0.2	---	---	---
PSOC-450	---	3.6	---	---	4.6	---	7.3	5.7	---
DJR-70	---	---	---	---	---	---	---	---	---
DJR-29	---	---	0.7	---	---	0.7	---	3.0	---
PSOC-535	---	---	---	0.8	0.7	1.4	---	---	---
PSOC-418	---	---	---	0.3	---	---	---	---	---
PSOC-623	---	---	---	0.2	---	---	---	---	---
PSOC-95	---	---	---	0.7	---	---	---	---	---
DJR-37 (POC-339)	---	---	---	---	---	---	---	---	---
DJR-39 (POC-340)	---	---	---	---	---	---	---	2.6	---

Table 1. (continued)

Sample	328 (23.11)	294 (23.11)	308 (23.58)	254 (23.89)	368 (24.31)	254 (24.72)	308 (25.08)
DJR-71 (PSOC-256)	---	---	0.2	---	---	---	---
DJR-67 (PSOC-330)	---	---	---	---	---	---	---
PSOC-349	---	---	---	---	---	---	---
PSOC-124	---	---	---	---	---	---	---
PSOC-372	---	---	0.8	---	---	---	---
PSOC-308	---	---	---	---	---	---	---
PSOC-641	---	---	---	---	---	---	---
DJR-47	---	---	---	---	0.7	---	0.6
DJR-44	---	---	---	---	---	---	---
PSOC-582	---	---	---	---	---	---	---
PSOC-399	---	---	2.9	---	0.4	---	---
DJR-69 (PSOC-405)	---	---	4.4	---	1.8	---	1.0
PSOC-155	---	---	---	---	---	---	---
PSOC-453	---	---	0.8	---	3.2	---	---
PSOC-459	---	---	---	---	---	---	---
PSOC-500	---	---	---	---	---	---	---
PSOC-503	---	---	---	---	---	---	---
DJR-66 (PSOC-312)	---	---	2.0	---	0.2	---	0.2
PSOC-450	---	---	---	---	0.7	---	1.8
DJR-70	---	---	---	---	---	---	---
DJR-29	---	---	3.8	---	---	---	---
PSOC-535	6.4	---	---	---	1.3	---	---
PSOC-418	---	---	---	---	1.8	---	1.0
PSOC-623	44.6	---	---	1.9	---	30.6	---
PSOC-95	---	---	0.6	---	---	---	---
DJR-37 (POC-339)	---	---	---	---	---	---	---
DJR-39 (POC-340)	---	---	0.1	---	---	---	---

Table 2. Mass Spectra of Oxidation Products

m/e	P-	% Base Peak
MW = 136	Benzoic Acid	
136	---	34
105	31	100
77	59	55
51	85	16
MW = 158	Cis-2-methylbutenedioic Acid	
127	31	100
99	59	17
59	99	17
MW = 162	2-Hydroxybutanedioic Acid	
131	31	7
113	49	9
103	59	100
72	90	91
61	101	34
59	103	17
MW = 162	Benzenepropenoic Acid	
162	---	45
131	31	100
103	59	43
77	85	28
51	111	9

Table 2. (continued)

m/e	P-	% Base Peak
MW = 176	2-Methoxybutanedioic Acid	
117	59	100
101	75	60
85	91	60
75	101	5
69	107	25
59	117	29
MW = 192	Phthalide-3-carboxylic Acid	
192	---	1
148	44	4
133	59	100
120	72	3
105	87	13
77	115	13
51	141	4
MW = 194A	Benzene-1,2-dicarboxylic Acid	
194	---	7
163	31	100
135	59	8
133	61	8
103	91	7
92	102	12
76	118	25

Table 2. (continued)

m/e	P-	% Base Peak
MW = 194B	Benzene-1,4-dicarboxylic Acid	
194	---	18
163	31	100
135	59	24
120	64	9
119	65	7
104	90	12
103	91	17
76	118	14
50	144	5
MW = 194C	Benzene-1,3-dicarboxylic Acid	
194	---	17
163	31	100
135	59	30
120	74	9
119	75	8
104	90	5
103	91	11
76	118	16
50	144	4
MW = 195	Pyridine-x,y-dicarboxylic Acid	
195	---	36
164	31	100

Table 2. (continued)

m/e	P-	% Base Peak
136	59	47
104	91	21
78	117	8
77	118	12
59	136	5
50	145	9
MW = 202A	2-Carboxybutenedioic Acid	
171	31	100
143	59	7
115	87	25
101	101	10
75	127	12
69	133	24
59	143	46
53	149	21
MW = 202B	x,y-Dicarboxybutanelide	
143	59	43
115	87	100
103	99	16
85	117	22
83	149	33
59	143	49
55	147	78

Table 2. (continued)

m/e	P-	% Base Peak
MW = 204	2-Carboxybutanedioic Acid	
173	31	16
145	59	79
112	92	100
101	103	22
85	119	5
59	145	21
55	149	26
MW = 207	3-Nitrobenzenepropanoic Acid	
176	31	9
161	46	22
148	59	26
130	77	45
119	88	29
102	105	53
92	115	100
77	130	67
65	142	87
59	148	41
51	156	47

Table 2. (continued)

m/e	P-	% Base Peak
MW = 208	Anthraquinone	
208	---	74
180	28	83
152	56	100
126	82	17
76	132	63
63	145	12
50	158	20
MW = 208	2-Carboxybenzeneacetic Acid	
208	---	58
177	31	100
149	59	39
147	61	24
106	102	21
91	117	76
90	118	26
89	119	37
78	130	14
65	143	12
MW = 209	3-Carboxypyridine-2-acetic Acid	
209	---	3
178	31	34
150	59	57

Table 2. (continued)

m/e	P-	% Base Peak
147	62	47
121	88	64
120	89	46
93	116	100
92	117	47
91	118	22
65	144	14
59	150	17
MW = 210	4,5,6,7-Tetrahydrophthalide-3-acetic Acid	
210	---	42
179	31	43
178	32	50
147	63	100
119	91	68
91	119	11
63	147	9
MW = 216A	3-Carboxy-2-pentenedioic Acid	
185	31	17
157	59	53
155	61	37
149	67	100
147	69	64
115	101	16

Table 2. (continued)

m/e	P-	% Base Peak
97	119	28
59	157	30
55	161	29
MW = 216B	x,y-Dicarboxypentenolide	
157	59	47
129	87	100
115	101	20
97	119	51
59	157	91
55	161	79
MW = 218A	3-Carboxypentanedioic Acid	
187	31	34
153	65	17
127	91	100
126	92	56
113	105	18
99	119	38
95	123	25
85	133	79
80	138	34
59	159	91
55	163	39

Table 2. (continued)

m/e	P-	% Base Peak
MW = 218B	Oxiranetricarboxylic Acid	
187	31	4
159	59	14
141	77	14
137	81	12
115	103	34
75	143	16
69	149	59
59	159	100
MW = 220	2-Hydroxybutanedioic Acid	
161	59	21
129	91	18
101	119	100
88	132	16
69	151	22
59	161	91
57	163	25
55	165	12
MW = 232	x-Carboxyhexanedioic Acid	
173	59	83
163	69	38
145	87	9
131	101	18

Table 2. (continued)

m/e	P-	% Base Peak
129	103	16
117	115	28
113	119	39
85	147	29
83	149	46
59	173	100
58	174	28
55	177	25
MW = 234	x-Carboxy-y-hydroxypentanedioic Acid	
175	59	8
143	91	100
101	133	91
59	175	36
57	177	12
55	179	5
MW = 239	Pyridine-2,x,y-tricarboxylic Acid	
239	---	1
208	31	100
162	77	79
150	89	8
147	92	8
134	105	9
129	110	9

Table 2. (continued)

m/e	P-	% Base Peak
103	136	9
75	164	25
MW = 250	x-Carboxyphthalide-3-carboxylic Acid	
250	---	56
219	31	100
218	32	72
203	47	12
192	58	10
160	90	14
147	103	50
132	118	45
104	128	17
75	175	7
MW = 252A	Benzene-1,2,4-tricarboxylic Acid	
252	---	6
221	31	100
193	59	14
191	61	9
162	90	25
161	91	14
147	105	5
135	117	16
119	133	30

Table 2. (continued)

m/e	P-	% Base Peak
103	149	36
75	177	24
MW = 252B	Benzene-1,2,3-tricarboxylic Acid	
221	31	100
175	77	8
149	103	16
120	132	10
119	133	12
104	148	37
76	176	21
75	177	14
MW = 253	Pyridine-x,y,z-tricarboxylic Acid	
232	31	34
195	58	100
194	59	22
165	88	18
137	116	49
59	194	12

Table 2. (continued)

m/e	P-	% Base Peak
MW = 254	Lactone of 2'-hydroxybiphenyl-2x-dicarboxylic Acid	
254	---	49
233	31	100
195	59	25
167	87	20
139	115	83
113	141	8
111	143	9
89	165	9
70	184	8
63	191	12
MW = 264	x-Carboxyphthalide-3-acetic Acid	
233	31	100
190	74	41
162	102	99
161	103	47
132	132	12
104	160	25
103	161	21
75	189	32
74	190	25

Table 2. (continued)

m/e	P-	% Base Peak
MW = 268	x-Carboxy-4,5,6,7-tetrahydrophthalide-3-acetic Acid	
268	---	30
237	31	38
236	32	54
223	45	13
222	46	18
205	63	100
195	73	53
194	74	24
176	92	24
165	103	25
163	105	78
137	131	72
105	163	17
104	164	16
59	209	10
MW = 274	x,y-Dicarboxy-2-pentenedioic Acid	
215	59	46
187	87	12
183	91	78
155	119	100
115	159	18
113	161	34

Table 2. (continued)

m/e	P-	% Base Peak
101	173	29
59	215	18
55	219	14
MW = 276A	2,3-Dicarboxypentanedioic Acid	
217	59	12
212	64	20
185	91	28
184	92	26
153	123	100
132	144	20
126	150	10
113	163	20
59	217	21
MW = 276B	Oxiranetetracarboxylic Acid	
245	31	28
217	59	5
189	87	39
173	103	49
161	115	22
133	143	45
127	149	63
105	171	99
83	193	60

Table 2. (continued)

m/e	P-	% Base Peak
74	202	39
69	207	43
59	217	100
MW = 290	x,y-Dicarboxyhexanedioic Acid	
259	31	37
199	91	43
198	92	82
167	123	42
166	124	47
139	151	100
114	176	29
113	177	18
107	183	45
59	231	32
55	235	8
MW = 297	Pyridine-2,x,y,x-tetracarboxylic Acid	
266	31	29
238	59	5
205	92	10
178	119	25
162	135	100
161	136	24
147	150	10

Table 2. (continued)

m/e	P-	% Base Peak
134	163	10
104	193	10
105	194	10
85	212	16
76	221	26
75	222	53
71	226	37
62	235	10
57	240	37
MW = 308	x,y-Dicarboxyphthalide-3-carboxylic Acid	
277	31	55
276	32	82
217	91	12
190	118	21
167	141	25
149	159	100
57	251	9
MW = 310A	Benzene-1,2,4,5-tetracarboxylic Acid	
310	---	12
280	30	39
279	31	100
251	59	9
177	133	13

Table 2. (continued)

m/e	P-	% Base Peak
162	148	26
161	149	20
MW = 310B	Benzene-1,2,3,5-tetracarboxylic Acid	
280	30	14
279	31	100
162	148	13
161	149	8
103	207	7
75	235	5
MW = 311	Pyridine-2,x,y,z-tetracarboxylic Acid	
280	31	53
279	32	93
252	59	10
249	62	12
223	88	33
195	116	94
163	148	100
59	252	8
MW = 322	x,y-Dicarboxyphthalide-3-acetic Acid	
290	32	10
279	43	37
262	60	68
249	73	100

Table 2. (continued)

m/e	P-	% Base Peak
231	91	20
221	101	13
167	155	18
149	173	99
119	203	10
104	218	10
59	263	34
57	265	17
55	267	21
MW = 326	x,y-Dicarboxy-4,5,6,7-tetrahydrophthalide-3-acetic Acid	
326	---	33
295	31	67
294	32	92
264	62	41
263	63	100
236	90	88
232	94	33
206	120	30
178	148	67
149	177	13
147	179	14
146	180	38
118	208	38

Table 2. (continued)

m/e	P-	% Base Peak
91	235	16
77	249	9
59	267	6
MW = 328	Acenaphthene-1,2,5-tricarboxylic Acid	
297	31	6
270	58	28
269	59	100
254	74	14
223	105	33
207	121	33
195	133	13
179	149	16
167	161	18
163	165	28
151	177	38
149	179	45
119	209	18
59	269	76
MW = 368	Benzene-1,2,3,4,5-pentacarboxylic Acid	
338	30	30
337	31	100
291	77	7
220	148	8

Table 2. (continued)

m/e	P-	% Base Peak
162	206	16
104	264	8

Table 3. Mass Spectra of Model Compounds

m/e	P-	% Base Peak
MW = 136 Benzoic Acid		
136	---	34
105	31	100
77	59	55
51	85	16
MW = 162 Benzenepropenoic Acid		
162	---	45
131	31	100
103	59	43
77	85	28
51	111	9
MW = 194A Benzene-1,2-dicarboxylic Acid		
194	---	7
163	31	100
135	59	8
133	61	8
103	91	7
92	102	12
76	118	25

Table 3. (continued)

m/e	P-	% Base Peak
MW = 194B	Benzene-1,4-dicarboxylic Acid	
194	---	18
163	31	100
135	59	24
120	64	9
119	65	7
104	90	12
103	91	17
76	118	14
50	144	5
MW = 194C	Benzene-1,2-dicarboxylic Acid	
194	---	17
163	31	100
135	59	30
120	74	9
119	75	8
104	90	5
103	91	11
76	118	16
50	144	4

Table 3. (continued)

m/e	P-	% Base Peak
MW = 204	2-Carboxybutanedioic Acid	
173	31	16
145	59	79
112	92	100
101	103	22
85	119	5
59	145	21
55	149	26
MW = 208	Anthraquinone	
208	---	74
180	28	83
152	56	100
126	82	17
76	132	63
63	145	12
50	158	20
MW = 218A	3-Carboxypentanedioic Acid	
187	31	34
153	65	17
127	91	100
126	92	56
113	105	18
99	119	38

Table 3. (continued)

m/e	P-	% Base Peak
95	123	25
85	133	79
80	138	34
59	159	91
55	163	39
MW = 252A	Benzene-1,2,4-tricarboxylic Acid	
252	---	6
221	31	100
193	59	14
191	61	9
162	90	25
161	91	14
147	105	5
135	117	16
119	133	30
103	149	36
75	177	24
MW = 252B	Benzene-1,2,3-tricarboxylic Acid	
221	31	100
175	77	8
149	103	16
120	132	10
119	133	12

Table 3. (continued)

m/e	P-	% Base Peak
104	148	37
76	176	21
75	177	14
MW = 276A	2,3-Dicarboxypentanedioic Acid	
217	59	12
212	64	20
185	91	28
184	92	26
153	123	100
132	144	20
126	150	10
113	163	20
59	217	21
MW = 310A	Benzene-1,2,4,5-tetracarboxylic Acid	
310	---	12
280	30	39
279	31	100
251	59	9
177	133	13
162	148	26
161	149	20

Table 3. (continued)

m/e	P-	% Base Peak
MW = 310B	Benzene-1,2,3,5-tetracarboxylic Acid	
280	30	14
279	31	100
162	148	13
161	169	8
103	207	7
75	235	5
MW = 368	Benzene-1,2,3,4,5-pentacarboxylic Acid	
338	30	30
337	31	100
291	77	7
220	148	8
162	206	16
104	264	8

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